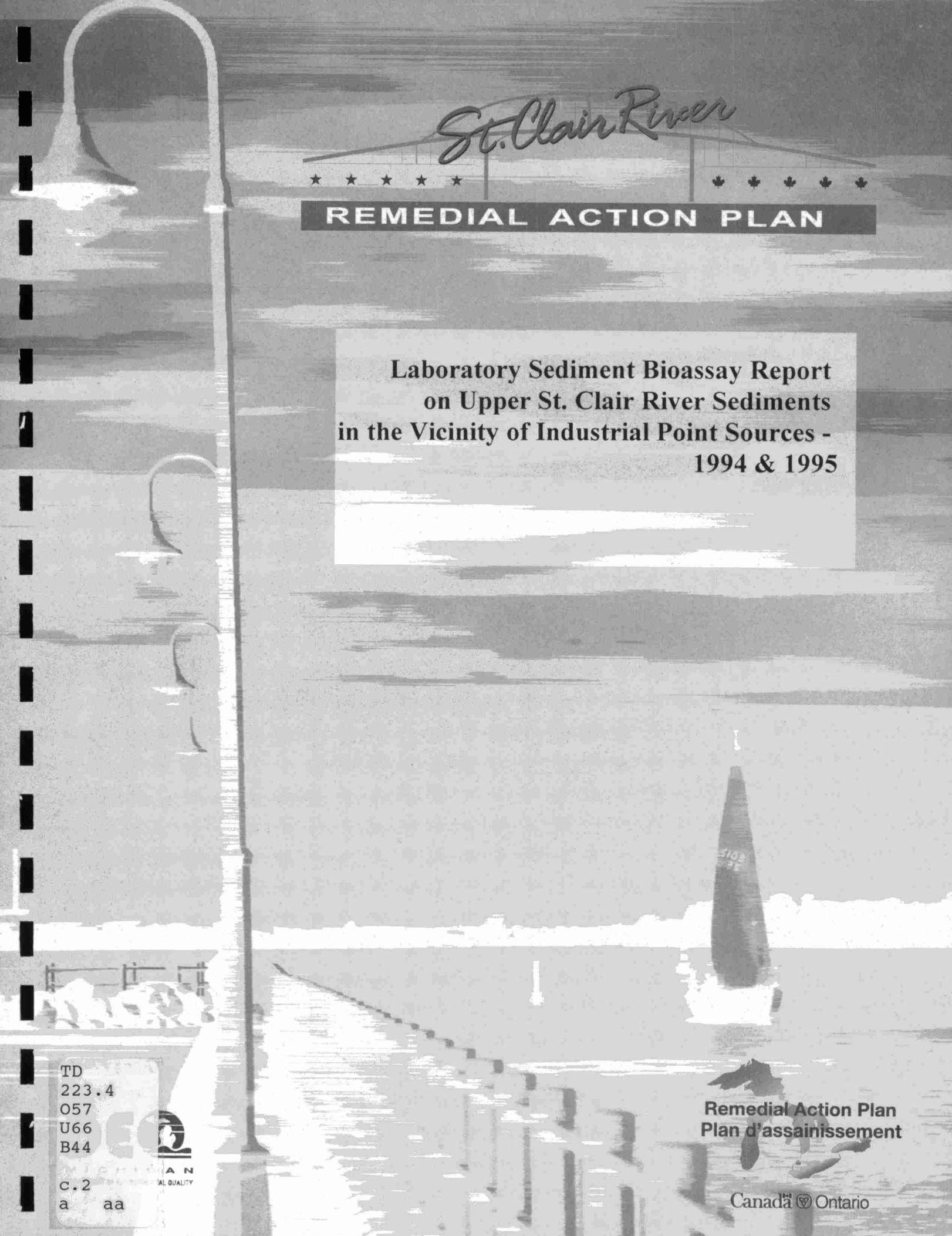


Laboratory Sediment Bioassay Report on Upper St. Clair River Sediments in the Vicinity of Industrial Point Sources - 1994 & 1995

Remedial Action Plan
Plan d'assainissement

Canada Ontario

ISBN 0-7778-6039-2

LABORATORY SEDIMENT BIOASSAY REPORT ON UPPER ST. CLAIR RIVER SEDIMENTS IN THE VICINITY OF INDUSTRIAL POINT SOURCES 1994 & 1995

FEBRUARY 1997

Cette publication technique
n'est disponible qu'en anglais.

LABORATORY SEDIMENT BIOASSAY REPORT

ON UPPER ST. CLAIR RIVER SEDIMENTS IN THE VICINITY

OF INDUSTRIAL POINT SOURCES 1994 & 1995

Prepared by:

D. Bedard and S. Petro
Ontario Ministry of Environment and Energy
Standards Development Branch
125 Resources Road
Etobicoke, Ontario

Prepared for:

P. Kauss
Environmental Monitoring and Reporting Branch

FEBRUARY 1997

ACKNOWLEDGEMENTS

The authors wish to thank Mark Whelley, Christy Hoeptig and Cindy Pammer for their valuable technical assistance in conducting the laboratory sediment bioassays. The authors gratefully acknowledge the staff of the OMOEE Laboratory Services Branch for providing chemical analysis of the sediment and biota samples.

Special thanks to the following OMOEE staff for their helpful review comments, Peter Kauss and Rein Jaagumagi, Environmental Monitoring and Reporting Branch, and Keith Somers, Science and Technology Branch.

EXECUTIVE SUMMARY

Sediments in the upper St. Clair River were sampled in spring 1994, fall 1994 and spring 1995, as part of an assessment in characterizing the potential ecological impacts of contaminated sediments for this Area of Concern. A total of 39 sites were collected along 13 transects in the vicinity of ESSO (Imperial Oil), the Cole Drain, Polysar Rubber Corporation and Dow Chemical Canada Inc., near Sarnia, Ontario. Sediments in this area are known to contain numerous organic compounds, particularly chlorinated hydrocarbons, as well as mercury.

An objective of this study was to assess the spatial and temporal pattern of sediment toxicity and chemical bioaccumulation using static, laboratory sediment toxicity tests. Three independent toxicity tests were performed on whole-sediment samples. Mortality, growth and avoidance behaviour of the burrowing mayfly, *Hexagenia limbata*, was measured in 21-day exposures. Chironomid (*Chironomus tentans*) growth and mortality was determined in 10-day tests. Mortality and chemical uptake by the fathead minnow, *Pimephales promelas*, was examined by a standard 21-day test.

Overall, the toxicity test results illustrated a high variability in organism toxicity on a spatial scale while temporal trends remained fairly constant. Among the test sediments, four sites were found to be lethal to all three test species and the sediments were collected downstream of industrial discharge points. One site was collected downstream of the ESSO intake (Stn 44-30), two stations situated downstream of the Cole Drain (Stns 136-10 and 136-30) and a single site downstream of Dow 1st street sewer (Stn 95-37). Another six stations were found to be either highly toxic ($\geq$ 70% mortality) or moderately toxic ($\geq$ 40% and $<$ 70% mortality) to both benthic invertebrates. The stations were 44-45, 73-30, 45-35, 46-25, 74-30 and 48-37. There was excellent agreement between *Hexagenia* and *Chironomus* mortality endpoints in identifying differences in sediment quality among sites. Substrate physical and nutrient characteristics were not considered to have a direct negative effect on either midge or mayfly biological endpoints. Minnow lethality was not significantly correlated with either mayfly or midge survival. A higher sensitivity of fish to elevated un-ionized ammonia concentrations during the test, may have played a role at some locations.

Petroleum-based substances are inferred as the principle toxicants in sediments from ESSO, the Cole Drain and Polysar. Total petroleum hydrocarbon sediment concentrations above 1500 μg/g (dry weight), were most frequently associated with higher organism toxicity. Significant correlations were measured between midge and mayfly lethality against the sum of hexachlorobenzene, hexachlorobutadiene, octachlorostyrene and pentachlorobenzene bulk sediment concentrations for the Dow sediments. The derived 10-day LC50 sediment concentration for the midge, *Chironomus*, was 147 μg/g (dry weight) and 162 μg/g for the mayfly, *Hexagenia*. These values are similar to those predicted using a critical body residue concentration of 1.0 to 1.6 mM/kg (wet weight), in conjunction with equilibrium partitioning-based sediment concentrations, for nonpolar narcotic substances. The toxicological action of these combined chemicals appear to be additive. The more lipophilic compounds measured in the sediment were also found to accumulate in the fathead minnow to the greatest extent. Chemical data indicate that the toxicological effect of highly volatile substances including hexachloroethane, chlorotoluene and trichlorobenzene could not be adequately assessed due to losses incurred during sediment manipulation prior to testing.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

1.0 INTRODUCTION

In May-June 1994, the Environmental Monitoring and Reporting Branch of the Ontario Ministry of Environment and Energy (OMOEE) carried out a detailed study of the upper St. Clair River sediments in the vicinity of ESSO (Imperial Oil), Polysar Rubber Corporation and Dow Chemical Canada Inc. plants near Sarnia, Ontario. The purpose of the investigation was to determine the detailed extent of sediment contamination and effects on ambient water quality, benthic community structure, chemical bioaccumulation and laboratory toxicity effects as outlined in the project description by Kauss (1994a).

The study was in response to an assessment conducted by the OMOEE in 1990 to identify and characterize the potential ecological impacts associated with contaminated sediment. Based on the 1990 studies, which covered the entire length of the St. Clair River, three priority impact zones were identified for further sediment characterization (Tarandus, 1992; Bedard and Petro, 1992a) by the St. Clair River RAP/BPAC Sediment Task team (MDNR and OMOEE, 1995). One of the recommendations put forth was to conduct further studies in each of the priority areas in order to assist the RAP Implementation committee in making decisions regarding site remediation. The study results confirmed that sediments collected from several sites in the upper St. Clair River were contaminated with a number of inorganic (copper, mercury, zinc) and organic compounds (chlorinated benzenes and toluenes, octachlorostyrene, hexachlorobutadiene). Some of these chemicals are persistent and bioaccumulative and have been related to a degradation of the benthos, exceed Severe Effect Level concentrations of the Provincial Sediment Quality Guidelines (Persaud *et al.*, 1992), lethal to benthic invertebrate and forage fish in laboratory toxicity tests, available for uptake by juvenile fathead minnows and are listed as banned substances in the province (OMOEE and MDNR, 1993).

In Fall 1994 and Spring 1995, additional surveys of the upper St. Clair River sediments were conducted in order to reassess the biological impacts associated with bottom sediments and to determine the temporal variability in sediment toxicity and chemical bioaccumulation. Another aim of the fall 1994 study was to satisfy required quality assurance objectives. The targeted sites were previously included in the spring 1994 survey. Ontario Ministry of Environment and Energy, Standards Development Branch assisted in the environmental assessment of surficial sediment quality by examining the association between inorganic and organic contamination and biological effects using documented laboratory sediment toxicity test procedures (Bedard *et al.*, 1992).

Whole-sediment toxicity tests were conducted for 39 field locations collected along 13 transects in 1994 and at four of these locations in 1995, using the mayfly nymph, *Hexagenia limbata* (21-day exposure, survival and growth), the midge larvae, *Chironomus tentans* (10-day exposure, survival and growth) and the juvenile fathead minnow, *Pimephales promelas* (21-day exposure, survival and chemical bioaccumulation). The battery of sediment toxicity tests provides a number of endpoints using organisms representing different trophic levels in order to measure differences in sediment quality. The laboratory toxicity tests provide a cost-effective technique for determining if sediment-associated contaminants are harmful to benthic organisms or are being released into the water-column. In conjunction with appropriate control sediments, spatial differences in sediment quality, the relative availability of contaminants and

their potential impacts can be ascertained. Sediment contaminant concentrations were based on field samples for the 1994 study and in 1995, chemical analysis was based on samples prepared for laboratory toxicity testing, as well as concurrent field-collected sediment. The sediment was analyzed for particle size, nutrients, metals, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), chlorinated organics, total petroleum hydrocarbons, solvent extractables and pesticides. Tissue analysis of surviving fathead minnows were submitted for total PCBs, chlorinated organics, pesticides and 16 PAH compounds, on single samples, where feasible.

2.0 MATERIALS AND METHODS

2.1 Sample Collection and Site Description

During May-June 1994, surficial sediment was collected at all 39 locations (transects 134 through 96; listed in order from upstream to downstream), that were designated by OMOEE, EMRB for sediment bioassays (Kauss, 1994a; Table 1). The test sediments were collected along 13 transects (3 different stations per transect) extending from the Canadian shore at varying distances. Exact placement of the station depended in part on the visual characterization of the substrate. The presence of fine-grained particles indicative of depositional areas served as a key selection criterion. This increased the likelihood of testing areas of higher contamination, increased comparability among sites and thereby reduced substrate-related interference of the toxicity data. In November 1994, repeat collections were made for stations along transects 95 and 136 (Stns 95-10,-30,-37 and Stns 136-10, -20, -30) on split samples, in order to conduct replicated toxicity tests and verify the level of toxicity observed in the spring samples. In May 1995, sediment was obtained at four locations situated at or near the original locations tested in 1994 and selected based on the availability of indigenous benthic fauna. The sites included a single location on each of four different transects (Stns 134-15, 47-15, 74-20 and 95-37) (Kauss, 1995a). Toxicity tests were completed on three discrete field replicates per location. At Stn 47-15, two sets of triplicate field samples were obtained.

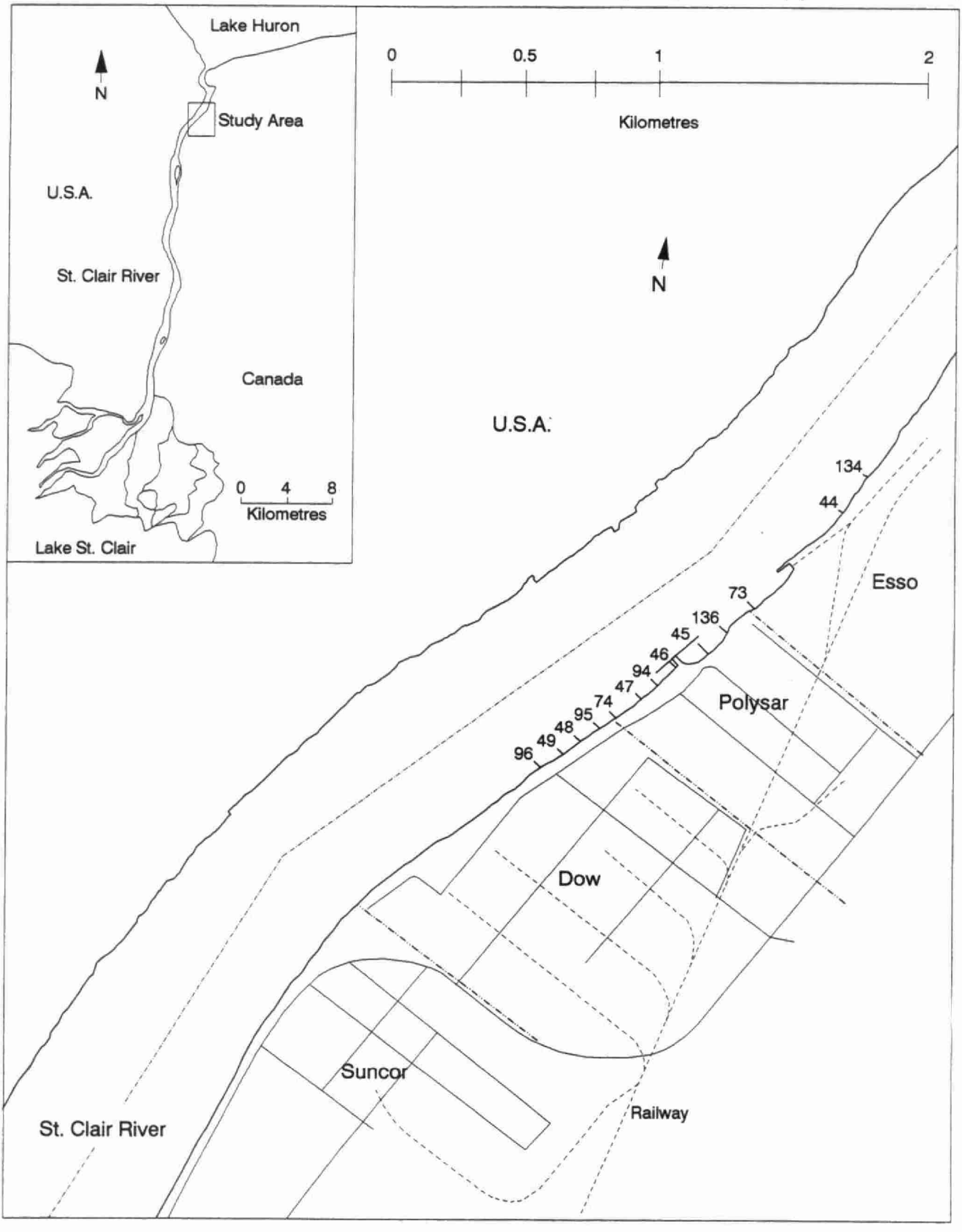
For each study, collection was done by diver using a 9" X 9" stainless-steel Ekman dredge. At each station, approximately 6-10 L of composited surficial sediment (top 5 cm) was collected from several grabs, depending upon the level of laboratory replication. The composited sediment was placed into 20 L plastic buckets lined with food-grade polyethylene bags and transported to the Toronto, Ontario laboratory where they were stored at 4°C until required.

Based on earlier investigative studies, a sampling grid was prepared for the upper St. Clair River. The test sediments were collected in an area extending from downstream of the ESSO intake (transect 44), around the Cole Drain (transect 73 and 136), along the Polysar property (transects 45, 46, 94, 47, and 74) and in the vicinity of the Dow 1st St and 2nd St sewers (transects 95, 48, 49 and 96) (Figure 1). The station locations are designated numerically by the distance measured in metres from the Canadian shoreline. On average, sediment was collected approximately 10 to 20 metres from shore and 10 to 20 metres apart, and the exact coordinates for each site are listed in Table 1 (Kauss, 1994a). Additional

TABLE 1. 1994 and 1995 St. Clair River Sampling Station Locations and Descriptions (Kauss 1994a)

Station				
Station Transect Number	Transect Location	Metres from shore	UTM Northing	UTM Easting
0134 (18)	just upstream of Imperial Oil (Esso) intake; between two red brick buildings	15	4756667.3	383895.1
"	"	25	4756675.3	383889.1
"	"	35	4756683.4	383883.2
0044 (--)	downstream of Esso intake and upstream of Esso BIOX plant discharge	15	4756461.0	383784.4
"	"	30	4756473.1	383775.5
"	"	45	4756485.1	383766.5
0073 (20)	upstream of Cole Drain and Polysar fence; off first building N. of fence with brown roof	10	4756136.2	383560.4
"	"	20	4756144.2	383554.4
"	"	30	4756152.3	383548.5
0136 (IS 9)	just downstream of Cole Drain discharge; upstream of first crib	10	4756027.9	383449.7
"	"	20	4756035.9	383443.7
"	"	30	4756044.0	383437.8
0045 (--)	inside N. end of Polysar dock & off stack; upstream of Polysar 54" sewer	5	4755917.2	383380.1
"	"	20	4755929.2	383371.1
"	"	35	4755941.3	383362.2
0046 (--)	inside S. end of Polysar dock; ~95 m downstream of Polysar 54" sewer	7	4755827.6	383239.8
"	"	15	4755834.0	383235.6
"	"	25	4755842.0	383229.6
0094 (IS 12)	at S. end of Polysar dock; ~200 m downstream of Polysar 54" sewer	10	4755779.7	383210.9
"	"	25	4755791.7	383201.9
"	"	40	4755803.8	383193.0
0047 (--)	opposite Polysar flare; upstream of Polysar 66" & 72" sewers	15	4755714.6	383155.8
"	"	35	4755730.7	383143.9
"	"	55	4755746.7	383131.9
0074 (22)	downstream of small Polysar (storm?) sewer; ~2 m above Polysar-Dow fence	5	4755615.1	383044.9
"	"	20	4755627.1	383035.9
"	"	30	4755635.1	383029.9
0095 (IS 14)	~50 m downstream of Dow 1st St. sewer; off first white sign on railing	10	4755582.8	383003.8
"	"	30	4755598.5	382991.4
"	"	37	4755604.1	382987.1
0048 (--)	downstream of Dow 1st St. sewer; off third white sign on railing	10	4755532.3	382948.2
"	"	25	4755544.2	382939.0
"	"	37	4755553.7	382931.7
0049 (--)	downstream of Dow 1st St. sewer; off fifth white sign on railing	10	4755486.0	382892.3
"	"	25	4755498.4	382883.8
"	"	40	4755510.9	382875.4
0096 (IS 15)	downstream of Dow 2nd St. sewer; off third tree at shoreline	22	4755404.9	382772.2
"	"	28	4755409.9	382769.1
"	"	35	4755415.4	382764.9

Figure 1: 1994 / 1995 Station Locations for Sediment Sampling in the Upper St. Clair River.



information obtained on the depth and sediment characteristics for each sample is described elsewhere (Kauss, 1994b).

In the spring of 1994 and 1995, a reference control sediment was sampled upstream of the Imperial Oil Ltd. intake (transect 134). The reference control sediment should be representative of naturally occurring background contamination levels for the study area and be physically similar to the test sediments to help discriminate effects due to physical or chemical causes. Sediment collected from Honey Harbour in Georgian Bay, Ontario, served as a negative control for each bioassay. The negative control sediment is a relatively uncontaminated sediment that provides a measure of test acceptability. Both control sediments are a basis for comparing the biological responses from the test sediments.

2.2 Analytical Methods

Chemical analysis of sediment and biota samples was carried out by the OMOEE, Laboratory Services Branch, located in Toronto. Routine test methods is described in the *OMOE Handbook of Analytical Methods for Environmental Samples* (OMOE, 1983). Quality assurance procedures included method blanks, spikes, duplicates and standard reference materials. Analytical detection limits for each of the sediment and tissue parameters are listed in Table A1.

Sediment Nutrients and Particle Size Characterization

Homogenized bulk sediment (< 2 mm fraction) was measured for total phosphorus (TP), total Kjeldahl nitrogen (TKN) and percent weight loss on ignition (LOI) which measured approximate organic content. Sediment total organic carbon (TOC) was determined with a LECO carbon analyzer using a dry combustion technique which oxidized carbon to CO_2. Particle size was measured on 50 g, air-dried samples using a Microtrac particle size analyzer for the size range 1.00 mm to 0.1 μm. This was to provide data for %sand (2mm -62 μm), %silt (62- 3.7 μm) and %clay (3.7 - 0.1 μm) size classes. Detailed test methodology is described in OMOEE (1995a; 1995b).

Trace Metals in Sediment

Prepared sediment samples were digested using a concentrated aqua-regia acid mixture (1 part HNO_3 to 3 parts HCl). The dissolved trace metals including As, Cd, Cr, Cu, Fe, Pb, Mn, Ni and Zn in the digestates were detected by inductively coupled argon plasma atomic emission spectroscopy (ICP-AES) and Hg by flow injection vapour generated flameless atomic absorption spectroscopy (AAS). Detailed test methodology is described in OMOEE (1994a).

Organic Chemicals in Sediment

Moist sediment samples were extracted with acetone and dichloromethane. The extract was

transferred to a rotary evaporator, concentrated and fractionated on a Florisil column. Different solvent combinations were used to elute the extracts into three groups, Fraction A1 contained total PCBs, 5 Aroclor groups, hexachlorobenzene, heptachlor, aldrin, octachlorostyrene, pp-DDE and mirex. Fraction A2 contained a- & b-BHC, a- & b-chlordane, op-DDT, pp-DDD, pp-DDT and fraction A3 included heptachlor epoxide, oxychlordane, dieldrin, endosulfan I & II, endosulfan sulphate, endrin and methoxyclor. Analytes were identified and quantified using capillary gas chromatography equipped with a Ni^{63} electron capture detector (GLC-ECD). Detailed test methodology is described in OMOEE (1994b; 1994c).

Organic Chemicals and Percent Lipid in Biota

Pooled whole fish samples (~5 g) were thawed, homogenized and acid digested using a concentrated hydrochloric acid (HCl) on single samples per transect. The digestate was reacted with a mixture of 25% dichloromethane in hexane. The extract was treated with sodium bicarbonate to ensure neutralization and dried with anhydrous sodium sulphate. Dichloromethane-cyclohexane was added to the evaporated samples, followed by clean-up and detected by capillary gas chromatography equipped with a mass selective detector. Final results are reported on a wet weight basis for 16 PAH compounds, 14 chlorinated organic compounds and 14 pesticides. Percent lipid was determined on an aliquot (25 ml) of the final extract obtained prior to clean-up. The solvent was allowed to evaporate by air-drying in a fumehood for 24 hours and lipid residues were measured. Detailed test methodology is described in OMOE (1990).

2.3 Laboratory Biological Testing Methods

Basic Experimental Design

Sediment biological tests were conducted according to OMOEE standardized procedures (Bedard *et al.*, 1992) and are briefly described below. The bioassays were static, single-species tests using whole-sediment. The experimental unit was a 1.8 L test chamber containing prepared sediment and dechlorinated municipal tap water (1:4, v:v). The chambers were randomly placed into a holding tank at ambient room temperature and maintained under a 16:8 hour, light:dark photoperiod and continuous aeration.

Moist field-collected bottom sediment was pressed through a 2-mm stainless-steel sieve to remove existing large biota and debris prior to use. Subsamples of this homogenized sediment were submitted for chemical and physical characterization according to standard OMOEE procedures for the 1995 samples only (OMOE, 1989). Sediment chemistry was based on the field 0 - 5 cm section of core samples that were collected concurrently with the sediment utilized in the laboratory toxicity tests for the 1994 studies. The sieved sediment was homogenized with a spatula and stored in 4 L acid-rinsed glass jars until required. Three hundred and twenty-five millilitre aliquots of homogenized sediment were placed into the test chamber and overlaid with the test water. After settling overnight, the chambers were aerated continuously until the termination of the test. A clean, negative control sediment that was collected from Honey Harbour, Georgian Bay, was used for each bioassay. Control mortality

must not exceed 15% for mayflies and fathead minnows and 25% for chironomids or the test is declared invalid.

Water in the exposure chambers was regularly monitored for pH, conductivity, total ammonia, un-ionized ammonia and dissolved oxygen. Dead organisms were removed and the numbers recorded on a daily basis. Any signs of abnormal behaviour of the test organisms or changes in appearance of the test chambers were noted. Water loss due to evaporation was replenished as needed. At the conclusion of the test, fathead minnow test organisms were collected, placed into glass vials and frozen prior to analysis. The whole body tissue samples were measured for percent lipid, 16 PAH compounds, 14 chlorinated organic compounds and 14 pesticides on single samples in the 1994 study. Similar analysis was not completed in 1995 due to the incurred high mortality of minnows during testing.

Hexagenia limbata Lethality and Growth Assay

The tests used 4 month old laboratory reared mayfly nymphs with an average wet weight of 6.06 mg ± 0.77 (s.e.) (n=35); 6.05 mg ± 0.75 (s.e.) (n=31) and 4.82 mg ± 0.40 (s.e.) (n=37), for the spring 1994, fall 1994 and 1995 toxicity tests, respectively. The nymphs were raised from eggs collected by Dr. J. Ciborowski at the University of Windsor, Windsor, Ontario. Mayflies were reared according to OMOEE procedures (Bedard *et al.*, 1992) and methods described in the literature (Friesen, 1981).

The rearing procedure involved the transfer of 600 newly-hatched nymphs to a 6.5 L aquarium which contained 2 cm of autoclaved sediment and 5.6 L dechlorinated tap water. Animals were maintained at ambient room temperature, 16:8 hour, light:dark photoperiod, constant aeration and fed a vegetable diet.

Test organisms were retrieved from the rearing aquaria by sieving small portions of sediment in a 500-μm mesh brass sieve. The nymphs were washed into an enamelled tray which held a fine mesh sieve and aerated, dechlorinated water. A Pasteur pipette (5-mm opening) was used to transfer the mayflies into 100 mL beakers of water and the contents were gently poured into the test chambers. Three laboratory replicates were run for each Station in the fall 1994 sediment bioassay. The spring 1994 and 1995 toxicity tests were conducted without laboratory replication. In each study, ten nymphs were added per jar, for a period of 21 days. Animals were not fed during the length of the test.

At the end of the test, the contents of each test chamber were emptied and rinsed in a sieve bucket. Surviving animals were counted and transferred to 150 mL beakers holding 100 mL dechlorinated water. The nymphs were immobilized with Alka-Seltzer®, blotted dry and individuals weighed to the nearest 0.01 mg, placed in vials and stored in a freezer.

Chironomus tentans Lethality and Growth Assay

Each toxicity test used 10-12 day old, cultured chironomid larvae weighing an average wet weight less than 1 mg. The OMOEE continuously cultures *C. tentans* larvae from egg to

adult following standard methods (Bedard *et al.*, 1992, Mosher *et al.*, 1982, Townsend *et al.*, 1981). Egg masses were acquired from Dr. J. Giesy at Michigan State University, Lansing, Michigan and have been cultured for several generations in our laboratory.

Initially, the midges were reared in enamelled trays for a period of 10 to 12 days and then maintained in a 21 L aquarium containing 1.6 L of silica sand. The cultures were held at ambient room temperature with continuous aeration and under a 16:8 hour, light:dark photoperiod. The larvae were provided a vegetable diet *ad libitum*.

Second instar larvae were directly transferred from the enamelled rearing pans into the test chamber using the 5-mm opening of a Pasteur pipette. A total of 15 animals were added per chamber to each of the three replicates in the fall 1994 study and single test chambers were employed for the spring 1994 and 1995 studies. Animals were fed daily 30 mg of a Cerophyll®:Tetra Conditioning Vegetable® (3:2, w:w) diet.

After 10 days, the contents of the test chambers were emptied and washed in a sieve bucket. Surviving animals were sorted, removed and placed into 150 mL beakers holding 100 mL dechlorinated water and 15 mL silica sand. The larvae were counted, blotted dry and individuals weighed to the nearest 0.01 mg.

Pimephales promelas Lethality and Bioaccumulation Assay

The spring 1994 test was completed in two phases as a result of animal availability. The first set of tests consisted of sediment collected from transects 44, 45, 46, 47, 48 and 49 and used cultured, juvenile fathead minnows that weighed 334 mg ± 58 (s.e.) (n = 10) (wet weight). The second set of tests consisted of sediment from transects 73, 74, 94, 95, 96, 134 and 136 and used animals that weighed 276 mg ± 30 (s.e.) (n = 25). The starting wet weight for the fathead minnows used in the 1995 test was 417 mg ± 39 (s.e.) (n = 30). The minnows were cultured at the OMOEE laboratory and followed techniques which for the most part are US EPA procedures (USEPA, 1987) with minor revisions (Bedard *et al.*, 1992).

Cultures were maintained at 20°C in a flow-through dechlorinated water system and under a 16:8 hour, light:dark photoperiod. Breeders were kept in 60 L glass aquarium and eggs are laid on spawning tiles. The tiles were incubated in a 25°C water-bath and the developing larvae were transferred to 400 L fibreglass holding tanks. Larval fish were fed 48-hour old live brine shrimp while juveniles and breeders were provided frozen brine shrimp. Each size class was fed *ad libitum*.

Each test chamber received 10 juvenile minnows (single jars per sample for spring 1994 Phase I and II and one replicate per field replicate in the 1995 study). The minnows were sorted into 250 mL glass beakers in groups of five. The contents of the beakers were emptied into a small net and the minnows released into the test chamber.

The minnows were exposed for 21 days and fed Tetra Conditioning Vegetable® diet in an amount equivalent to 1% of the average starting wet weight, on a daily basis. After 21 days the surviving fathead minnows were pooled from each replicate, counted, immobilized

with Alka-Seltzer® and placed into 30 mL glass vials and frozen pending chemical analysis.

Reference Toxicant Testing

A water-only reference toxicity ($CuSO_4$) test was conducted with *H. limbata* and *C. tentans* for 48-hours and LC50s were calculated for each study. The static tests consisted of four test concentrations and a control. The nominal copper concentrations were 0.05, 0.25, 0.5, 1 and 3 mg/L. Ten mayfly nymphs or midge larvae were placed into each of four replicate 250 mL beakers. To help reduce stress, five glass tubes were placed into the mayfly test beakers and a fine layer of silica sand was added to the midge test containers. Mortality was monitored every 24 hours and water quality parameters were taken at 0 and 48 hours. The mayfly test used 4 month old laboratory reared mayfly nymphs with an average wet weight of 4.45 mg ± 0.5 (s.e.) for spring 1994; 6.69 mg ± 0.5 (s.e.) for fall 1994; and 4.81 ± 0.35 (s.e.) for 1995. The midge larvae were 10-12 day post-hatch with an average wet weight < 1 mg in each set of tests.

Bioassay Schedule for Spring 1994 Sediment Samples

Test Organism	Species	Starting Date ('94)	Completion Date ('94)	Test Duration
Mayfly	*Hexagenia limbata*	Tue. July 12	Tue. August 2	21 days
Chironomid	*Chironomus tentans*	Fri. August 5	Mon. August 15	10 days
Minnow	*Pimephales promelas*	Phase I Thur. August 18	Thur September 8	21 days
Minnow	*Pimephales promelas*	Phase II Wed. September 21	Wed. October 12	21 days

Bioassay Schedule for Fall 1994 Sediment Samples

Test Organism	Species	Starting Date ('94)	Completion Date ('94)	Test Duration
Mayfly	*Hexagenia limbata*	Tue. December 6	Tue December 27	21 days
Chironomid	*Chironomus tentans*	Tue. December 6	Fri. December 16	10 days
Minnow	*Pimephales promelas*	Not Tested		

Bioassay Schedule for Spring 1995 Sediment Samples

Test Organism	Species	Starting Date ('95)	Completion Date ('95)	Test Duration
Mayfly	*Hexagenia limbata*	Tue. June 13	Tue. July 4	21 days
Chironomid	*Chironomus tentans*	Tue. June 20	Fri. June 30	10 days
Minnow	*Pimephales promelas*	Tue. June 13	Tue. July 4	21 days

2.4 Statistical Methods

Statistical analyses were performed using the SAS® software package (SAS, 1985). Comparisons were made among the test and control sediments using One-Way Analysis of Variance (ANOVA) and Tukey's studentized range test (HSD) and planned comparisons (Steel and Torrie, 1960). Dunnett's one-tailed *t*-test was used solely to compare mortality between the control and test sediments and the associated minimum significant difference (MSD) was described as a measure of test sensitivity. Analysis was made on arc-sine transformed mortality data. Homogeneity of variance across groups was tested using Bartlett's test. Coefficients of variation (C.V. %) were calculated for each endpoint as a measure of test precision. Spearman rank correlation analysis was used to investigate the correlation among the different biological endpoints for each species and sediment characteristics. Simple linear regression was used to measure the strength of the relationship between chemical and biological variables. Kendall's tau-b coefficients were used to assess the degree of concordance between the biological data for 1994 and 1995. LC50's (including the associated 95% confidence limits) were calculated using software developed by Stephan (1977) and were derived by probit analysis.

3.0 RESULTS

3.1 Water Quality Test Parameters

Conductivity, pH, total ammonia, un-ionized ammonia and dissolved oxygen parameters were periodically measured on the overlying water for each test species in each of the three studies and summarized in Tables 2, 2A and 2B. Values are reported as mean ± standard deviation. Similar pH and conductivity water quality measurements were recorded among the test sites, regardless of test species or study. For the reference control and test sites, pH averaged from 7.8 to 8.3 and conductivity from 416 to 532 umho/cm. Dissolved oxygen within the test jars remained above acceptable levels (>4 mg/l) throughout the test (OMOEE,

TABLE 2. Mean (± s.d.) water quality characteristics in spring 1994 sediment bioassays.

Test Organism: Mayfly (Hexagenia limbata)[a]			Test Temperature: 19.2°C (0.7)[d]		
Transect	*pH*	*D.O.* mg/L	*Conductivity* umho/cm	*Total Ammonia* mg/L	*Un-ionized Ammonia* mg/L
Control	7.68 (.18)	8.8 (0.4)	316 (10)	<0.10	<0.003
Reference (134)	8.12 (.10)	8.7 (0.2)	437 (32)	1.79 (1.20)	0.087
Stn 44	7.91 (.25)	7.8 (.13)	450 (55)	3.00 (2.39)	0.084
Stn 73	8.10 (.08)	8.7 (0.7)	400 (24)	0.64 (0.28)	0.028
Stn 136	8.07 (.22)	8.4 (1.0)	458 (39)	4.57 (3.19)	0.213
Stn 45	8.16 (.06)	8.9 (0.3)	417 (24)	1.01 (0.62)	0.056
Stn 46	8.18 (.06)	8.9 (0.3)	480 (71)	1.31 (1.70)	0.052
Stn 94	8.13 (.06)	8.8 (0.2)	458 (63)	2.22 (3.12)	0.101
Stn 47	8.15 (.06)	8.9 (0.3)	432 (40)	2.16 (2.09)	0.127
Stn 74	8.11 (.14)	8.9 (0.3)	435 (42)	1.69 (2.01)	0.062
Stn 95	8.08 (.06)	8.8 (0.3)	522 (117)	3.74 (1.44)	0.137
Stn 48	8.11 (.12)	8.5 (0.6)	442 (30)	3.36 (2.60)	0.171
Stn 49	8.06 (.13)	8.5 (0.5)	421 (24)	2.31 (1.39)	0.112
Stn 96	8.12 (.09)	8.8 (0.2)	417 (12)	0.97 (1.50)	0.037
Test Organism: Midge (Chironomus tentans)[b]			Test Temperature: 19.5°C (0.9)		
Transect	*pH*	*D.O.* mg/L	*Conductivity* umho/cm	*Total Ammonia* mg/L	*Un-ionized Ammonia* mg/L
Control	7.79 (.12)	9.0 (0.5)	326 (7)	<0.10	<0.003
Reference (134)	8.01 (.17)	9.1 (0.1)	421 (19)	1.56 (0.34)	0.053
Stn 44	8.13 (.07)	8.9 (0.1)	444 (29)	2.66 (1.32)	0.109
Stn 73	8.17 (.08)	9.0 (0.3)	413 (44)	0.89 (0.33)	0.046
Stn 136	8.16 (.07)	9.1 (0.4)	444 (37)	3.87 (1.09)	0.201
Stn 45	8.04 (.07)	9.0 (0.9)	418 (37)	1.24 (0.29)	0.044
Stn 46	7.98 (.22)	8.7 (0.2)	463 (101)	2.07 (1.43)	0.050
Stn 94	8.15 (.02)	9.2 (0.2)	439 (55)	2.78 (2.73)	0.094
Stn 47	8.07 (.13)	9.1 (0.2)	428 (49)	1.44 (1.33)	0.080
Stn 74	7.83 (.19)	8.7 (0.4)	427 (37)	2.29 (2.90)	0.052
Stn 95	8.03 (.15)	9.1 (0.1)	480 (80)	1.54 (0.87)	0.053
Stn 48	7.99 (.14)	8.9 (0.2)	441 (40)	2.95 (1.15)	0.088
Stn 49	8.00 (.14)	8.4 (0.2)	435 (43)	2.40 (1.00)	0.088
Stn 96	8.16 (.02)	9.2 (0.5)	428 (32)	1.53 (1.24)	0.055

a Sample size N=4; b Sample size N=3; d Based on daily recorded temperature measured during the test period.

Underlining indicates un-ionized ammonia concentrations that exceed the PWQO of 0.02 mg/L

TABLE 2. ...Continued.

Test Organism: Minnow (Pimephales promelas)[c] Test Temperature: 19.4° (0.6)[d]
Phase I

Transect	*pH*	*D.O.* mg/L	*Conductivity* umho/cm	*Total Ammonia* mg/L	*Un–ionized Ammonia* mg/L
Control	7.07 (.22)	8.4 (0.5)	344 (30)	0.15 (0.18)	<0.003
Stn 44	7.81 (.16)	8.2 (0.7)	512 (54)	3.47 (1.77)	0.070
Stn 45	7.80 (.20)	8.0 (1.2)	489 (68)	3.26 (2.74)	0.068
Stn 46	7.81 (.20)	8.7 (0.4)	519 (78)	2.51 (1.68)	0.070
Stn 47	7.75 (.24)	8.0 (0.7)	497 (80)	3.24 (2.21)	0.074
Stn 48	7.88 (.19)	8.3 (0.4)	520 (70)	4.58 (3.74)	0.127
Stn 49	7.92 (.20)	8.6 (0.2)	525 (80)	4.57 (4.14)	0.191

Test Organism: Minnow (Pimephales promelas)[c] Test Temperature: 18.4°C (1.5)
Phase II

Transect	*pH*	*D.O.* mg/L	*Conductivity* umho/cm	*Total Ammonia* mg/L	*Un–ionized Ammonia* mg/L
Control	7.67 (.38)	9.2 (0.5)	336 (63)	0.28 (0.43)	0.013
Reference (134)	8.04 (.20)	9.2 (0.4)	487 (65)	1.63 (1.75)	0.049
Stn 73	7.89 (.21)	8.9 (0.4)	436 (88)	0.95 (0.72)	0.024
Stn 136	8.06 (.25)	9.3 (0.7)	491 (53)	2.26 (2.07)	0.100
Stn 94	8.11 (.14)	9.2 (0.6)	497 (77)	3.29 (1.79)	0.148
Stn 74	7.90 (.30)	8.0 (1.9)	517 (94)	3.01 (1.62	0.090
Stn 95	8.03 (.08)	9.3 (0.7)	563 (117)	2.62 (1.20)	0.088
Stn 96	8.03 (.19)	9.3 (1.3)	480 (67)	1.28 (0.85)	0.041

c Sample size N=5;

d Based on daily recorded temperature measured during the test period.

Underlining indicates un–ionized ammonia concentrations that exceed the PWQO of 0.02 mg/L

TABLE 2A. Mean (± s.d.) water quality characteristics in fall 1994 sediment bioassays.

Test Organism: Mayfly (Hexagenia limbata)[a]			Test Temperature: 20.6°C (0.3)[c]		
Station	*pH*	*D.O.* mg/L	*Conductivity* umho/cm	*Total Ammonia* mg/L	*Un-ionized Ammonia* mg/L
Control	8.09 (.04)	9.0 (0.3)	289 (11)	<0.10	<0.003
Stn 136-10	8.24 (.12)	8.6 (1.0)	432 (33)	<0.10	0.005
Stn 136-20	8.28 (.13)	9.0 (0.2)	423 (30)	<0.10	0.004
Stn 136-30	8.25 (.07)	8.9 (0.2)	422 (26)	<0.10	<0.003
Stn 95-10	8.31 (.13)	9.1 (0.2)	395 (16)	<0.10	0.005
Stn 95-30	8.22 (.07)	8.9 (0.2)	430 (26)	0.17 (0.09)	0.010
Stn 95-37	8.23 (.08)	9.0 (0.2)	403 (26)	0.13 (0.06)	0.009
Test Organism: Midge (Chironomus tentans)[b]			Test Temperature: 20.5°C (0.3)		
Station	*pH*	*D.O.* mg/L	*Conductivity* umho/cm	*Total Ammonia* mg/L	*Un-ionized Ammonia* mg/L
Control	7.93 (.34)	8.3 (0.3)	307 (4)	<0.10	<0.003
Stn 136-10	8.21 (.17)	8.6 (0.3)	431 (40)	0.16 (0.09)	0.009
Stn 136-20	8.27 (.08)	8.7 (0.4)	418 (36)	0.29 (0.25)	0.019
Stn 136-30	8.21 (.08)	8.4 (0.1)	423 (31)	0.11 (0.06)	0.006
Stn 95-10	8.22 (.04)	8.5 (0.4)	405 (34)	0.20 (0.14)	0.010
Stn 95-30	8.18 (.13)	8.2 (0.7)	425 (50)	0.23 (0.21)	0.009
Stn 95-37	8.16 (.26)	7.3 (2.4)	399 (26)	0.20 (0.14)	0.009

a Sample size N=4; b Sample size N=3.

c Based on daily recorded temperature.

TABLE 2B. Mean (± s.d.) water quality characteristics in 1995 sediment bioassays.

Station	pH	D.O. mg/L	Conductivity umho/cm	Total Ammonia mg/L	Un-ionized Ammonia mg/L
Test Organism: Mayfly (Hexagenia limbata) [a]		Test Temperature: 20.0°C (1.1)			
Control	7.96 (.08)	8.9 (0.1)	308 (8)	<0.10	<0.003
Reference (134)	8.34 (.05)	8.8 (0.2)	451 (40)	1.38 (1.29)	0.123
Stn 47-35 Rep 1	8.29 (.10)	8.5 (0.1)	481 (55)	2.95 (2.94)	0.224
Stn 47-35 Rep 2	8.33 (.07)	8.6 (0.2)	485 (68)	2.55 (2.40)	0.225
Stn 74-20	8.28 (.07)	8.5 (0.3)	479 (71)	2.55 (2.89)	0.187
Stn 95-34	8.25 (.19)	8.7 (0.4)	434 (42)	0.78 (0.42)	0.047
Test Organism: Midge (Chironomus tentans) [b]		Test Temperature: 20.5°C (0.8)			
Control	7.98 (.14)	8.8 (0.2)	335 (11)	0.20 (0.10)	0.007
Reference (134)	8.26 (.21)	8.4 (0.3)	444 (33)	4.06 (2.31)	0.356
Stn 47-35 Rep 1	8.34 (.09)	8.4 (0.2)	489 (71)	7.66 (3.88)	0.645
Stn 47-35 Rep 2	8.36 (.12)	8.4 (0.3)	485 (63)	6.93 (3.10)	0.717
Stn 74-20	8.37 (.03)	8.8 (0.1)	476 (54)	8.26 (2.58)	0.845
Stn 95-34	8.25 (.01)	8.9 (0.1)	445 (37)	1.64 (1.19)	0.121
Test Organism: Minnow (Pimephales promelas) [c]		Test Temperature: 20.0°C (1.0)			
Control	7.30 (.39)	8.1 (0.3)	334 (29)	1.98 (1.91)	0.024
[d] Reference (134)	8.28 (.12)	7.9 (0.1)	527 (123)	15.32 (12.20)	1.323
[d] Stn 47-35 Rep 1	8.26 (.17)	8.0 (0.2)	530 (111)	16.57 (11.00)	1.529
Stn 47-35 Rep 2	8.08 (.33)	8.0 (0.4)	528 (105)	13.79 (12.40)	0.895
Stn 74-20	7.94 (.34)	7.3 (1.3)	531 (88)	18.56 (10.13)	0.797
Stn 95-34	8.25 (.07)	8.1 (0.4)	548 (127)	21.28 (18.19)	1.509

a Sample size N=4; b Sample size N=3; c Sample size N=5; d Sample size N=4.

Underlining indicates un-ionized ammonia concentrations that exceed the PWQO of 0.02 mg/L.

1994d). Test temperature was at or near 20°C for each bioassay.

Total ammonia and converted un-ionized ammonia readings exhibited the greatest variability both temporally and spatially. The spring 1994 data was based on measurements pooled across a transect and only general observations can be made on a spatial scale (Table 2). The occurrence of an elevated reading at any particular station would be dampened in the overall un-ionized ammonia calculation. A similar level of average un-ionized ammonia was reported across the mayfly, midge and minnow assays (Range: 0.07 to 0.10 mg/L). Interestingly, the prolonged storage of sediments used in the minnow Phase II study of four weeks, did not appear to markedly affect ammonia readings.

Site-to-site differences in un-ionized ammonia can be more thoroughly examined from the fall 1994 and 1995 toxicity tests, where replicate measurements were available for each station tested. In fall 1994, un-ionized ammonia concentrations did not vary among stations along transect 136 or transect 95 nor between these two transects (Table 2A). This may, in part, reflect the similarity among stations along a transect, in terms of sediment physical and nutrient characteristics (see Table 3). These test sediments had some of the lowest TOC values (< 17 mg/g) among the 39 stations collected in spring 1994. Particle size was also fairly consistent among stations along a transect.

Comparison between the 1994 spring and late fall samples for transects 136 and 95 did reveal a substantial reduction in un-ionized ammonia levels. For example in the midge assay, for transect 136, average un-ionized ammonia concentrations dropped from 0.20 to 0.01 mg/L. A five fold reduction in un-ionized ammonia was reported for transect 95, i.e., 0.05 to 0.009 mg/L. Similar trends were noted in the mayfly toxicity tests. Seasonal factors such as temperature could have a profound influence on natural bacterial metabolic rates in the sediments, thereby altering the ammonia concentrations between the June and late November 1994 sediment collections (Sarda and Burton, 1995).

The spring 1995 data also tends to support the importance of temporal differences in ammonia concentrations. Average un-ionized ammonia concentrations in the overlying water for all sediments, except the negative control, substantially exceeded the water quality objective in the mayfly, midge and minnow toxicity tests (Table 2B). Average un-ionized ammonia measurements for the minnow toxicity test was the highest at 1.20 mg/L NH_3, followed by an average reading of 0.53 mg/L in the midge assay. Readings were similar among the test sediments relative to the upstream reference sediment, suggesting a common factor contributing to the elevated ammonia for the study area. The affinity of ammonia levels among the three test organisms further implies that the sediment is acting as the likely common source of the ammonia problem.

3.2 Sediment Characterization

Detailed sediment chemistry results for both 1994 and 1995 field samples are reported by Kauss (1995b) and the following sections summarize the sediment physical and chemical parameters to aid in the interpretation of the biological toxicity results. For positional reference of the transects, major industrial point sources are used in the data tables. Chemical

analysis is based either on field surficial sediment (1994 samples) and/or on the sediment prepared for toxicity testing (1995 samples). The latter approach is preferred because the data is based on a subsample that is removed from the prepared, sieved sediment samples directly used in the laboratory toxicity tests. Given the large number of samples collected in 1994 and the analytical cost involved, it was decided that the field sample chemistry would be used for the interpretation of the 1994 toxicity results. Every attempt was made to ensure that the field chemistry samples were collected in a similar manner and at the same location as those samples collected for sediment toxicity testing. Any discrepancies between the relative chemical distribution between field-collected and laboratory-tested samples can be gleaned from a small number of sediment samples from the 1995 survey.

Physical and Nutrient Properties

Sediments were characterized for % sand (2mm-62μm), % silt (62-3.7μm), % clay (3.7-0.1μm), % loss on ignition (%LOI), total organic carbon (TOC), total phosphorus (TP) and total Kjeldahl nitrogen (TKN) (Tables 3; 3A).

The 1994 field sediment samples covered a wide range of particle-size distributions and nutrient conditions (Table 3). The surficial sediments appeared to be characteristic of a high-energy, riverine system, with over 85% of the test sediments containing at least 50% sand-sized particles. Total organic carbon was generally low, < 20 mg/g, at 66% of the sites but was interspersed with pockets of organically-enriched sediments, even within the same transect. Total Kjeldahl nitrogen values ranged from 0.3 to 2.0 mg/g.

Among the test sediments, there was a strong negative correlation between % sand and TOC ($r = -.45$; $p < .004$), as well as TKN ($r = -.75$; $p < .00001$). In other words, the coarser the substrate, the more nutrient-poor the sediment. Both of these factors can have either a positive or negative influence on the toxicity results, particularly for the benthic species that are more dependent on the substrate for their livelihood. It was also evident that the reference sediment encompassed a range of substrate types in terms of particle size composition but had a narrow range in TOC concentrations, which should be fairly indicative of the physical characteristics of the test sediments and adequately reflect survival and growth effects due to minimal nutrient enrichment.

Physical and nutrient data for the 1995 sediment samples are reported in Table 3A for both the field sediment and sediment used in the laboratory toxicity tests for three test sites as well as the reference control station. The nutrient parameters were similar between the field and laboratory test samples at each site. The press-sieving of the sediment through a 2 mm screen did not diminish or increase the organic content of the sediment. Similarly, particle-size composition, which is based on the < 2 mm size fraction, would have completely passed through the 2 mm sieve. A difference in % sand and % fines was noted at Stn 74-20 between the field and test sediments, probably an indicator of the heterogeneity in sediment type encountered in the field. Sediments with a higher percentage of sand-sized particles (> 75%) had a corresponding lower TOC (< 9 mg/g). The remaining sites (Stns 47-35 and 74-20) had higher amounts of fine material and organic matter.

TABLE 3. Sediment physical and nutrient characteristics in control(s) and St. Clair River 1994 field sediment samples.

Transect	*Station Number* (m offshore)	*% Sand* (2mm – 62μm)	*% Silt & % Clay* (62 – 0.1μm)	*% LOI*	*TOC* mg/g	*TP* mg/g	*TKN* mg/g
Control		27.2	73.2	8.7	37	1.2	4.4
Reference	134 – 15	84.5	15.6	1.4	11	0.2	0.6
Upstream of ESSO	–25	76.5	23.5	1.8	12	0.2	0.8
	–35	15.0	85.0	1.6	10	0.2	0.7
Downstream of	44 – 15	83.1	16.9	1.3	9	0.2	0.6
ESSO intake above	–30	73.6	26.4	1.7	10	0.2	0.9
discharge	–45	66.7	33.3	1.6	13	0.2	0.6
Upstream of	73 – 10	89.5	10.5	1.4	2	0.1	0.3
Cole Drain	–20	18.3	81.6	2.2	14	0.2	0.6
	–30	0.0	100.0	2.4	15	0.4	0.8
Downstream of	136 – 10	79.8	20.2	1.9	17	0.3	0.5
Cole Drain	–20	70.4	29.6	1.8	12	0.2	0.6
discharge	–30	60.0	40.0	2.4	10	0.2	0.7
Upstream of Polysar	45 – 5	66.5	33.6	0.9	9	0.4	0.5
54" sewer	–20	77.3	22.7	5.6	81	0.3	0.7
	–35	48.5	51.5	6.4	97	0.7	1.0
95 m downsteam of	46 –7	68.6	31.2	6.2	47	0.3	1.0
Polysar 54" sewer	–15	83.3	16.5	5.6	43	0.4	0.7
	–25	35.9	64.1	6.8	48	0.3	0.9
200 m downstream	94 – 10	77.7	22.2	4.0	34	0.4	0.9
of Polysar 54" sewer	–25	51.3	48.6	3.7	30	0.4	1.5
	–40	92.0	8.0	1.5	13	0.2	0.5
Upstream of Polysar	47 – 15	64.8	35.1	1.6	19	0.2	0.7
66" and 72" sewers	–35	54.9	45.2	2.6	25	0.3	1.3
	–55	85.9	14.1	1.3	19	0.1	0.5
Downstream of	74 – 5	95.5	4.5	0.8	4	0.2	0.4
Polysar 66" and 72"	–20	45.0	55.0	5.3	28	0.5	2.0
sewers	–30	67.6	32.4	2.6	21	0.3	0.7
50 m downstream	95 – 10	95.4	4.6	0.4	4	0.1	0.4
of Dow 1st Street	–30	86.5	13.4	1.4	10	0.3	0.5
sewer	–37	92.1	7.9	1.9	16	0.2	0.4
Downstream of	48 – 10	66.6	33.5	6.5	8	0.1	0.6
Dow 1st Street	–25	58.8	41.2	3.4	25	0.3	1.3
sewer	–37	85.5	14.5	1.8	14	0.1	0.5
Downstream of	49 – 10	89.2	10.9	0.8	5	0.1	0.3
Dow 1st Street	–25	67.0	33.0	1.5	9	0.3	0.5
sewer	–40	86.2	13.9	1.3	8	0.2	0.3
Downstream of	96 – 22	91.3	8.7	1.1	4	0.1	0.4
Dow 2nd Street	–28	80.6	19.4	1.0	8	0.2	0.5
sewer	–35	85.2	14.8	3.0	24	0.2	0.6

TABLE 3A. Sediment physical and nutrient characteristics in St. Clair River 1995 laboratory bioassay and field sediment samples.

Station		*% Sand* (2mm – 62μm)	*% Silt & % Clay* (62 – 0.1μm)	*% LOI*	*TOC* mg/g	*TP* mg/g	*TKN* mg/g
Reference Upstream of ESSO	Bioassay Sediment	75.0	24.6	1.2	6	0.2	0.6
Stn 134 – 15	Field Sediment (Range)	81.0 (78–85)	18.5 (15–21)	1.3 (1.1–1.4)	9 (8–9)	0.1 (0.14–0.16)	0.7 (0.6–0.8)
Upstream of Polysar 66" and 72" sewers	Bioassay Sediment	29.0	70.8	3.6	24	0.7	2.3
Stn 47 –35	Field Sediment (Range)	36.3 (25–48)	63.0 (51–74)	4.3 (3.3–5.4)	25 (22–28)	0.4 (0.3–0.5)	1.9 (1.5–2.5)
Downstream of Polysar 66" and 72" sewers	Bioassay Sediment	25.0	74.1	3.6	25	0.4	1.6
Stn 74 – 20	Field Sediment (Range)	64.6 (63–66)	35.3 (33–37)	3.3 (3.2–3.5)	19 (18–20)	0.3 (0.2–0.3)	1.2 (1.2)
50 m Downstream of Dow 1st Street sewer	Bioassay Sediment	88.0	11.1	1.0	6	0.1	0.3
Stn 95 – 34	Field Sediment (Range)	97.6 (97–98)	2.1 (2.0–2.3)	0.6 (0.4–0.9)	4 (2–5)	0.1 (0.10–0.12)	0.4 (0.4–0.5)

Trace Metal Sediment Concentrations

Bulk sediment samples were analyzed for 11 trace metals (Tables 4; 4A). The sediment metal concentrations were compared to Severe Effect Level (SEL) and Lowest Effect Level (LEL) concentrations as outlined in the Provincial Sediment Quality Guidelines (PSQGs) (Persaud *et al.*, 1992). The SEL is defined as that chemical concentration in the sediment that is considered to be detrimental to the majority of the macrobenthos and the LEL is the sediment contaminant concentration which can be tolerated by most benthic species.

Chemical analysis of 1994 field sediments indicated that sediments downstream of Dow 1st St. sewer had the highest mercury contamination. Of these sites, transect 49 had the highest reported values, concentrations were 22 to 81 times higher than the PSQG-SEL guideline value of 2 μg/g (Range: 44 to 163 μg/g). Sediment Hg concentrations ranged from 1.6 to 60 μg/g along transects 95, 48 and 96. This area of high Hg contamination was also evident in previous sediment surveys. Historical maximum Hg sediment concentrations included 1470 μg/g in 1968 (OMOE, 1977), 58 μg/g in 1977 (OMOE, 1977), 51 μg/g during the 1980's (UGLCCS, 1988) and 15 μg/g in 1990 (Pope, 1993). Levels appear to be comparable to previous sediment concentrations and are related to point source loadings both past and present (UGLCCS, 1988). The majority of the remaining sediment metal concentrations were low and were similar to, or less than, the respective PSQG-LEL concentrations. In addition, concentrations were indicative of background sediment metal concentrations found for transect 134.

Table 4A provides metal sediment chemistry on sediments collected in 1995 for three test sites and the upstream control. Samples were submitted for three field replicates and a randomly selected sample of sediment prepared for sediment toxicity testing. Within-site sediment metal variability was generally low and sediment metal concentrations remained below PSQG-SEL concentrations. In addition, manipulation of the samples prior to toxicity testing appeared to have little or no influence on sediment metal concentrations. Sediment concentrations on the toxicity test samples fell within the range of concentrations indicative of field conditions on a total metal basis. Changes in the form or speciation of each metal or any alteration in acid-volatile sulphide concentrations was not addressed in this study. Comparison between 1994 and 1995 metal sediment concentrations for these select stations showed no significant change in metal distribution.

Since the Severe Effects-Level concentration was exceeded for Hg only and taking into account its' potential for bioaccumulation, the relationship between inorganic sediment concentrations and the biological data will focus on Hg only.

Organic Chemical Sediment Concentrations

Of the suite of organic compounds analyzed for in the 1994/95 field sediments, concentrations of 20 organochlorine pesticides in all sediment samples were below the respective detection limits (Table 5). Bulk sediment concentrations for total PCBs, total PAHs, total petroleum hydrocarbons, solvent extractables, total 2,3,7,8-tetraCDD toxicity equivalent concentrations (TEQ) for PCDDs and PCDFs, and 15 chlorinated organic compounds are

TABLE 4. Bulk concentrations of trace metals in St. Clair River 1994 field sediment samples (μg/g dry weight).

Transect	Station No. (m offshore)	Al%	As	Cd	Cr	Cu	Fe%	Hg	Mn	Ni	Pb	Zn
Reference Upstream of ESSO	134 – 15	0.3	3.8	0.4 <T	7	44	0.7	0.07	170	7	15	150
	–25	0.4	4.3	0.5 <T	11	130	0.8	0.05 <T	183	9	30	350
	–35	0.8	7.6	0.4 <T	16	57	1.6	0.02 <T	280	19	25	200
Downstream of ESSO intake above discharge	44 – 15	0.3	3.2	0.5 <T	8	21	0.6	0.12	160	7	11	58
	–30	0.3	3.6	0.3 <T	9	38	0.7	0.09	170	8	16	100
	–45	0.5	4.2	0.3 <T	12	29	1.0	0.06	180	9	32	110
Upstream of Cole Drain	73 – 10	0.3	4.1	0.3 <T	7	23	0.9	0.03 <T	160	8	18	78
	–20	0.6	5.6	0.5 <T	12	37	1.4	0.05 <T	300	17	28	66
	–30	1.3	6.0	0.6 <T	23	36	1.9	0.10	360	25	55	91
Downstream of Cole Drain discharge	136 – 10	0.9	7.4	0.8 <T	15	37	6.7	0.27	180	24	27	59
	–20	0.3	3.3	0.5 <T	8	23	0.7	0.10	180	9	11	64
	–30	0.4	3.9	0.8 <T	12	84	1.0	0.13	180	13	37	110
Upstream of Polysar 54" sewer	45 – 5	0.5	5.8	0.8 <T	14	20	4.1	0.27	200	21	26	37
	–20	0.6	8.1	1.0 <T	20	45	5.5	0.23	170	37	30	49
	–35	0.8	9.2	1.1	18	67	3.1	0.29	220	24	85	76
95 m downsteam of Polysar 54" sewer	46 –7	0.4	4.1	0.4 <T	11	20	1.2	0.29	170	13	17	52
	–15	0.3	3.9	0.3 <T	10	22	1.2	0.41	153	11	20	53
	–25	0.5	7.5	0.3 <T	15	46	2.1	0.99	180	16	53	110
200 m downstream of Polysar 54" sewer	94 – 10	0.4	4.9	0.4 <T	13	29	1.0	0.57	193	31	28	70
	–25	0.6	4.8	0.5 <T	13	28	1.3	0.21	206	16	18	69
	–40	0.3	3.9	0.3 <T	10	15	1.1	0.19	143	9	32	45
Upstream of Polysar 66" and 72" sewers	47 – 15	0.4	4.1	2.1	11	34	1.3	0.26	170	10	20	65
	–35	0.5	5.3	0.6 <T	12	25	1.2	0.07	210	14	16	72
	–55	0.3	4.6	0.5 <T	9	19	1.0	0.13	170	9	15	62
Downstream of Polysar 66" and 72" sewers	74 – 5	0.3	2.7	0.2 <W	22	15	0.6	0.77	140	7	62	46
	–20	0.8	6.8	0.7 <T	17	34	1.3	0.36	250	19	22	180
	–30	0.4	3.6	0.4 <T	15	58	0.9	0.66	190	12	23	93
50 m downstream of Dow 1st Street sewer	95 – 10	0.2	3.5	0.5 <T	11	24	1.0	5.20	130	12	9 <T	70
	–30	0.3	3.4	0.3 <T	10	25	1.0	6.26	186	10	15	76
	–37	0.3	3.6	0.5 <T	12	41	1.2	1.60	160	11	33	120
Downstream of Dow 1st Street sewer	48 – 10	0.3	3.4	0.2 <W	8	16	0.7	60.00	140	8	7 <T	46
	–25	0.5	4.9	0.5 <T	12	5	0.9	29.00	200	13	15	91
	–37	0.3	3.9	0.3 <T	12	30	1.3	2.70	150	8	17	76
Downstream of Dow 1st Street sewer	49 – 10	0.2	2.7	0.2 <T	18	13	0.6	163.00	130	12	10 <T	42
	–25	0.4	4.6	0.3 <T	9	30	1.1	84.00	180	10	17	56
	–40	0.3	3.7	0.3 <T	12	30	1.4	44.00	150	8	17	91
Downstream of Dow 2nd Street sewer	96 – 22	0.2	1.9	0.2 <T	8	11	0.7	13.00	150	6	8 <T	33
	–28	0.3	3.9	0.2 <T	10	21	0.9	24.00	170	8	6 <T	51
	–35	0.4	4.6	0.2 <T	11	58	1.2	24.00	150	22	26	72

Shading indicate sediment trace metal concentrations that exceed PSQG–SELs.
NA – Not Available; <W – Not Detected; <T –Trace Amount.

TABLE 4A. Bulk concentrations of trace metals in St. Clair River 1995 laboratory bioassay and field sediment samples (μg/g dry weight).

Station		Al%	As	Cd	Cr	Cu	Fe%	Hg	Mn	Ni	Pb	Zn
Reference	Bioassay											
Upstream of ESSO	Sediment	0.3	4.2	0.5 <T	8	51	0.7	0.06	180	8	14	130
	Field											
Stn 134 – 15	Sediment	0.3	4.2	0.2 <T	9	48	0.7	0.01 <W	176	10	15	146
	(Range)	(0.3–0.4)	(4.0–4.3)	(<W – <T)	(8–9)	(42–58)	(0.7)	(<W)	(170–180)	(8–14)	(14–18)	(140–160)
Upstream of Polysar	Bioassay											
66" and 72" sewers	Sediment	0.5	5.6	0.7 <T	13	30	1.3	0.15	235	15	14	69
	Field											
Stn 47 –35	Sediment	0.8	5.9	0.7 <T	17	28	1.4	0.07	266	19	18	77
	(Range)	(0.6–0.9)	(5.5–6.8)	(<T)	(16–20)	(27–32)	(1.3–1.6)	(<T–0.09)	(240–300)	(18–22)	(18)	(70–80)
Downstream of	Bioassay											
Polysar 66" and 72"	Sediment	0.5	5.2	0.6 <T	15	61	1.2	1.00	220	16	18	120
sewers	Field											
	Sediment	0.5	4.4	0.3 <T	13	37	1.1	0.48	210	15	18	106
Stn 74 –20	(Range)	(0.5)	(4.3–4.7)	(<W–<T)	(12–14)	(31–41)	(1.1–1.2)	(0.39–0.59)	(200–220)	(14–15)	(17–19)	(98–110)
50 m downstream	Bioassay											
of Dow 1st Street	Sediment	0.2	5.0	0.3 <T	7	23	0.8	0.58	120	6	20	99
sewer	Field											
	Sediment	0.2	2.8	0.3 <T	7	18	0.9	0.36	133	6	14	81
Stn 95 –34	(Range)	(0.2)	(2.6–3.1)	(<W–<T)	(7–8)	(16–20)	(0.8–10)	(0.29–0.47)	(120–140)	(6–7)	(10–20)	(70–100)

NA – Not Available; <W – Not Detected; <T –Trace Amount.

TABLE 5. Bulk sediment concentrations for chlorinated organics and pesticides in reference control and St. Clair River 1994 field sediment samples (ng/g, dry weight).

All Stations	Heptachlor	1 <W
	Aldrin	1 <W
	Mirex	5 <W
	a–BHC	1 <W
	b–BHC	1 <W
	g–BHC	1 <W
	a–Chlordane	2 <W
	g–Chlordane	2 <W
	Oxychlordane	2 <W
	op–DDT	5 <W
	pp–DDD	5 <W
	pp–DDT	5 <W
	pp–DDE	5 <W
	Methoxychlor	5 <W
	Heptachlor epoxide	1 <W
	Endosulphan I	2 <W
	Dieldrin	2 <W
	Endrin	4 <W
	Endosulphan II	4 <W
	Endosulphan sulphate	4 <W

<W – Not Detected.

reported in Tables 6 and 6A. Sediment chemical criteria is currently available for PCBs, PAHs and HCB only.

For the 1994 field samples, exceedence of the PSQG-SEL concentration occurred at one location for total PAHs (Stn 47-35) and at 16 sites for HCB (Transects 74, 95, 48, 49, 96 and Stn 136-30) (Table 6). Maximum HCB sediment concentration reached 490000 ng/g at Stn 95-30. Locations downstream had sediment HCB levels from 800 - 10500 ng/g.

Distribution of total PAHs and solvent extractables appear to be fairly ubiquitous with measurable levels noted at the upstream reference site. Total PAHs were present in the range of 200 - 34540 ng/g at all but one test site and solvent extractable sediment concentrations varied from 348 to 6374 ng/g. Total petroleum hydrocarbon sediment concentrations were on average one-half the reported solvent extractable concentrations. Total TEQ data indicate higher carcinogenic potency for PCDDs and PCDFs in sediments collected near Dow, with a mean value of 81.6 pg/g, and a mean value of 5.0 pg/g at the remaining upstream locations. A similar range in distribution for total TEQ has been reported previously for Detroit and St. Clair River surficial sediments (Kauss, 1994c).

Other organic chemicals that followed a widespread distribution in the test sediments yet were found below trace amounts in the reference sediment included, in order of decreasing concentrations, HCBD > HCB > OCS > QCB = 1,2,4-tCB > 1,3,5-tCB. The remaining organic compounds were generally elevated in sediments collected along Dow transects 95, 48, 49 and 96. The spatial pattern of sediment contamination generally conforms to known loadings from related industries in the area. For instance, the presence of high concentrations of HCBD, tCBs, QCB, HCB and OCS first appear downstream of the Cole Drain. The Cole Drain serves as a collector of leachate and runoff from several landfills and some of the highest net loadings of benzenes, HCBD and OCS have been reported at this source (OMOE, 1992a; MDNR and OMOEE, 1995). Further downstream, another increase in sediment chemical concentrations occurred for HCBD, 1,2,4-tCB and HCB, just below the Polysar 66" and 72" sewers. Polysar is a manufacturer of rubber compounds, produces and refines petrochemicals and its' point-source discharges contained elevated concentrations of CBs in 1989-91 (OMOEE, 1992a; EC and OMOE, 1986). Peak concentrations of HCBD, tCBs, teCBs, HCE, QCB, HCB and OCS were reported along the Dow waterfront. Dow has been a major manufacturer of chlorinated solvents and effluent loading data indicate the presence of HCB, OCS and other chlorinated organics according to recent MISA monitoring data (OMOEE, 1992a). Sediment HCB concentrations in 1994 are higher than those registered in earlier surveys (Max: 490 μg/g), suggesting continuing inputs. The maximum sediment HCB concentrations in the vicinity of the Dow 1st Street sewer in 1990 was 97 μg/g (Pope, 1993), in 1986, 110 μg/g (OMOE, 1991), and in 1984, 5 μg/g (EC and OMOE, 1986)

Results of chlorinated hydrocarbon analysis for the 1995 sediment samples are reported as an average and range of concentrations for the three discrete field replicates collected per station (Table 6A). In addition, data is reported on one of three field replicates that was collected for toxicity testing. Examination of the field data will provide information on the heterogeneity of in-situ organic chemistry and the laboratory toxicity sample chemistry affords an opportunity to measure the extent of change that may arise from the sieving, storage and homogenization of the sample prior to toxicity testing and the accuracy of the sampling technique used to obtain the sediment samples.

TABLE 6. Bulk concentrations of total polychlorinated biphenyls, total polycyclic aromatic hydrocarbons total 2,3,7,8–tetraCDD TEQ, solvent extractables, total petroleum hydrocarbons and chlorinated organics in St. Clair River 1994 field sediment samples.

Transect	*Station Number* (m offshore)	Total PCBs (ng/g, dry wt)	Total PAHs (ng/g, dry wt)	Total petroleum hydrocarbons (µg/g, dry wt)	Solvent Extractables (µg/g, dry wt)	Total 2378–TetraCDD TEQ (pg/g, dry wt)
Reference	134 – 15	20 <W	650	100 <W	674	0.1
Upstream of ESSO	–25	20 <W	2053	270	982	1.2
	–35	20 <W	420	100 <W	498	0.6
Downstream of	44 – 15	340	420	400	727	2.0
ESSO intake above	–30	20 <W	1640	300	967	0.9
discharge	–45	20 <W	900	450	678	0.1
Upstream of	73 – 10	20 <W	5380	200	591	0.5
Cole Drain	–20	20 <W	4553	800	1333	0.4
	–30	20 <W	5200	4000	4222	0.1
Downstream of	136 – 10	20 <W	3800	NA	1118	20
Cole Drain	–20	20 <W	2380	220	1058	0.6
discharge	–30	20 <W	8600	1700	2920	17
Upstream of Polysar	45 – 5	20 <W	200	100 <W	365	0.3
54" sewer	–20	20 <W	280	200	533	16
	–35	20 <W	11460	NA	5272	45
95 m downsteam of	46 –7	20 <W	2040	270	1335	1.9
Polysar 54" sewer	–15	40 <T	6113	200	933	0.4
	–25	140 <T	14780	1500	1585	2.6
200 m downstream	94 – 10	146 <T	4260	530	1921	0.4
of Polysar 54" sewer	–25	20 <W	4233	500	1872	1.3
	–40	20 <W	1580	100 <W	384	0.5
Upstream of Polysar	47 – 15	133 <T	5093	600	1104	1.1
66" and 72" sewers	–35	100 <T	436900	300	1431	1.1
	–55	20 <W	3120	100 <W	488	0.5
Downstream of	74 – 5	360	760	100 <W	522	1.5
Polysar 66" and 72"	–20	20 <W	5000	700	3034	3.2
sewers	–30	20 <W	34540	4100	6374	3.5
50 m downstream	95 – 10	1380	380	100 <W	348	21
of Dow 1st Street	–30	1180	1113	100 <W	923	40
sewer	–37	2340	6900	1000	2603	100
Downstream of	48 – 10	3500	1160	100 <W	921	56
Dow 1st Street	–25	1680	2300	NA	2278	64
sewer	–37	1900	17200	1200	5168	162
Downstream of	49 – 10	680	400	100 <W	619	21
Dow 1st Street	–25	920	1660	220	1258	244
sewer	–40	1200	2120	100 <W	1200	76
Downstream of	96 – 22	100 <T	540	100 <W	634	3.6
Dow 2nd Street	–28	520	1420	230	452	32
sewer	–35	1980	8520	1100	2526	161

< W – Not Detected; < T – Trace Amount; NA – Not Available.

Shading indicate sediment organic concentrations that exceed PSQG–SELs.

Total petroleum hydrocarbon concentration based on compounds with 15 to 50 carbon units.

TABLE 6. ...Continued.

Transect	*Station Number* (m offshore)	Hexa–chloro–ethane	Hexa–chloro–butadiene	2,3,6–tri–chloro–toluene	2,4,5–tri–chloro–toluene	2,6,a–tri–chloro–toluene	1,2,3–tri–chloro–benzene	1,2,4–tri–chloro–benzene
Reference	134 – 15	1 <W	11	1 <W	1 <W	1 <W	2 <W	20 <T
Upstream of ESSO	–25	2 <T	8 <T	1 <W	1 <W	1 <W	2 <W	23
	–35	1 <W	1 <W	1 <W	1 <W	1 <W	2 <W	2 <W
Downstream of	44 – 15	1 <W	94	1 <W	1 <W	1 <W	2 <W	28
ESSO intake above	–30	1 <W	33	1 <W	1 <W	1 <W	2 <W	23
discharge	–45	1 <W	1 <W	1 <W	1 <W	1 <W	2 <W	25
Upstream of	73 – 10	1 <W	3 <T	1 <W	1 <W	1 <W	2 <W	25
Cole Drain	–20	1 <W	7 <T	1 <W	1 <W	1 <W	2 <W	2 <W
	–30	1 <W	5 <T	1 <W	1 <W	1 <W	2 <W	3 <T
Downstream of	136 – 10	1 <W	380	1 <W	10 <T	1 <W	2 <W	130
Cole Drain	–20	1 <W	1800	1 <W	1 <W	1 <W	2 <W	118
discharge	–30	1 <W	875	1 <W	12	1 <W	2 <W	167
Upstream of Polysar	45 – 5	1 <W	210	1 <W	1 <W	1 <W	2 <W	41
54" sewer	–20	1 <W	3500	1 <W	1 <W	1 <W	2 <W	300
	–35	1 <W	900	1 <W	1 <W	1 <W	2 <W	230
95 m downsteam of	46 –7	1 <W	435	1 <W	1 <W	1 <W	2 <W	11 <T
Polysar 54" sewer	–15	8 <T	1014	1 <W	3 <T	1 <W	2 <W	42
	–25	20	912	1 <W	1 <W	1 <W	2 <W	170
200 m downstream	94 – 10	5 <T	167	1 <W	1 <W	1 <W	2 <W	2 <W
of Polysar 54" sewer	–25	1 <W	347	1 <W	1 <W	1 <W	2 <W	56
	–40	8 <T	846	1 <W	1 <W	1 <W	2 <W	78
Upstream of Polysar	47 – 15	6 <T	262	1 <W	1 <W	1 <W	2 <W	2 <W
66" and 72" sewers	–35	6 <T	338	5 <T	1 <W	1 <W	2 <W	2 <W
	–55	4 <T	1300	1 <W	1 <W	1 <W	2 <W	2 <W
Downstream of	74 – 5	1 <W	3480	1 <W	34	1 <W	2 <W	1400
Polysar 66" and 72"	–20	1 <W	4000	1 <W	1 <W	1 <W	2 <W	590
sewers	–30	1 <W	2000	1 <W	75	1 <W	2 <W	2800
50 m downstream	95 – 10	225	3400	20	1 <W	1 <W	40	1300
of Dow 1st Street	–30	556	27133	17	43	1 <W	14 <T	2123
sewer	–37	3100	114000	27	1 <W	1 <W	17 <T	6600
Downstream of	48 – 10	411	16600	5 <T	6 <T	1 <W	11 <T	1270
Dow 1st Street	–25	120	6700	5 <T	3 <T	62	9 <T	480
sewer	–37	1600	243000	108	19	1 <W	118	7000
Downstream of	49 – 10	154	4400	1 <W	13	1 <W	2 <W	83
Dow 1st Street	–25	552	4940	1 <W	1 <W	1 <W	2 <W	136
sewer	–40	727	55000	4 <T	54	1 <W	11 <T	1680
Downstream of	96 – 22	30	1430	1 <W	1 <W	1 <W	2 <W	62
Dow 2nd Street	–28	280	4000	30	88	1 <W	2 <W	253
sewer	–35	2400	13250	1 <W	1 <W	1 <W	12 <T	572
		1	2		3		4	4
Log Kow		4.62	4.90		4.78		4.04	3.98

< W – Not Detected; < T – Trace Amount. Unit of measurement is ng/g, dry weight.

1 Veith et al., 1979; 2 Banerjee, 1980; 3 Van Leeuwen et al., 1992; 4 Miller et al., 1985.

TABLE 6. ...Continued.

Transect	*Station Number* (m offshore)	1,3,5–tri–chloro–benzene	1,2,3,4–tetra–chloro–benzene	1,2,3,5–tetra–chloro–benzene	1,2,4,5–tetra–chloro–benzene	Penta–chloro–benzene	Hexa–chloro–benzene	Octa–chloro–styrene
Reference	134 – 15	2 <W	1 <W	1 <W	1 <W	1 <W	9 <T	1 <W
Upstream of ESSO	–25	2 <W	1 <W	1 <W	1 <W	4 <T	89	7 <T
	–35	2 <W	1 <W	1 <W	1 <W	1 <W	1 <W	1 <W
Downstream of	44 – 15	15 <T	1 <W	1 <W	1 <W	1 <W	20	1 <W
ESSO intake above	–30	2 <W	1 <W	1 <W	1 <W	1 <W	5 <T	1 <W
discharge	–45	2 <W	1 <W	1 <W	1 <W	1 <W	5 <T	1 <W
Upstream of	73 – 10	9 <T	1 <W	1 <W	1 <W	1 <W	6 <T	6 <T
Cole Drain	–20	15 <T	1 <W	1 <W	1 <W	1 <W	6 <T	6 <T
	–30	2 <W	1 <W	1 <W	1 <W	1 <W	12	1 <W
Downstream of	136 – 10	140	8 <T	30	1 <W	67	260	1130
Cole Drain	–20	14 <T	1 <W	14	1 <W	35	120	110
discharge	–30	167	1 <W	28	28	103	1100	5300
Upstream of Polysar	45 – 5	17 <T	1 <W	1 <W	1 <W	10	20	24
54" sewer	–20	190	15	20	20	200	400	660
	–35	215	15	20	20	83	200	3400
95 m downsteam of	46 –7	67	1 <W	5 <T	12	15	47	110
Polysar 54" sewer	–15	98	1 <W	6 <T	15	29	131	203
	–25	436	9 <T	32	69	55	121	1440
200 m downstream	94 – 10	28	1 <W	3 <T	7 <T	11	85	88
of Polysar 54" sewer	–25	64	1 <W	7 <T	21	22	209	216
	–40	40	1 <W	10 <T	13	29	75	124
Upstream of Polysar	47 – 15	32	1 <W	5 <T	12	17	79	485
66" and 72" sewers	–35	45	1 <W	11	27	33	205	160
	–55	37	3 <T	14	19	69	196	190
Downstream of	74 – 5	2 <W	48	62	62	95	450	110
Polysar 66" and 72"	–20	89	65	1 <W	1 <W	280	2000	800
sewers	–30	2 <W	1 <W	30	66	95	750	750
50 m downstream	95 – 10	83	120	180	140	270	1950	180
of Dow 1st Street	–30	75	170	100	291	6010	490000	27396
sewer	–37	1600	300	206	360	2450	180000	13000
Downstream of	48 – 10	323	1 <W	227	323	750	14900	1300
Dow 1st Street	–25	172	124	138	264	580	7400	2600
sewer	–37	427	1640	1276	1565	6500	105000	8600
Downstream of	49 – 10	200	22	67	157	290	6750	371
Dow 1st Street	–25	532	35	127	344	267	4570	485
sewer	–40	177	152	380	295	1590	41000	2750
Downstream of	96 – 22	86	1 <W	25	100	61	800	160
Dow 2nd Street	–28	307	62	102	335	325	6300	254
sewer	–35	130	110	130	327	560	5900	215
Log Kow		4 4.02	4 4.55	4 4.65	4 4.51	4 5.03	4 5.45	4 6.29

< W – Not Detected; < T – Trace Amount. Unit of measuremnet is ng/g, dry weight.

Shading indicate sediment organic concentrations that exceed PSQG–SELs.

4 Miller et al., 1985.

TABLE 6A. Bulk concentrations of total polychlorinated biphenyls and chlorinated organics in St. Clair River 1995 laboratory bioassay and field sediment samples (ng/g, dry weight).

Sample size: bioassay laboratory samples Stn 47–35 n=2, other Stns n=1; field samples n=3.

Station		Total PCBs	Hexachloro–ethane	Hexachloro–butadiene	2,3,6–trichloro–toluene	2,4,5–trichloro–toluene	2,6,a–trichloro–toluene	1,2,3–trichloro–benzene
Reference	Bioassay							
Upstream of ESSO	Sediment	20 <W	1 <W	200	1 <W	1 <W	NA	2 <W
	Field							
Stn 134 – 15	Sediment	20 <W	1 <W	11	1 <W	1 <W	1 <W	2 <W
	(Range)	(<W)	(<W)	(<T–22)	(<W)	(<W)	(<W)	(<W)
Upstream of Polysar	Bioassay							
66" and 72" sewers	Sediment	20 <W	1 <W	320	1 <W	1 <W	NA	2 <W
	Field							
Stn 47 –35	Sediment	20 <W	5 <T	566	1 <W	1 <W	1 <W	2 <W
	(Range)	(<W)	(<T)	(490–608)	(<W)	(<W)	(<W)	(<W)
Downstream of	Bioassay							
Polysar 66" and 72"	Sediment	20 <W	1 <W	680	1 <W	1 <W	NA	2 <W
sewers	Field							
	Sediment	20 <W	93	6005	1 <W	72	1 <W	2 <W
Stn 74 –20	(Range)	(<W)	(58–146)	(4472–7314)	(<W)	(<W–110)	(<W)	(<W)
50 m downstream	Bioassay							
of Dow 1st Street	Sediment	20 <W	1 <W	5700	1 <W	27	NA	2 <W
sewer	Field							
	Sediment	20 <W	708	48685	1 <W	95	57	2 <W
Stn 95 –34	(Range)	(<W)	(596–851)	(30270–65087)	(<W)	(88–107)	(35–71)	(<W)

Shading indicate sediment trace metal concentrations that exceed PSQG–SELs.

NA – Not Available; <W – Not Detected; <T –Trace Amount.

TABLE 6A. ...Continued.

Station		1,2,4–trichloro–benzene	1,3,5–trichloro–benzene	1,2,3,4–tetra–chlorobenzene	1,2,3,5–tetra–chlorobenzene	1,2,4,5–tetra–chlorobenzene	Pentachloro–benzene	Hexachloro–benzene	Octachloro–styrene
Reference Upstream of ESSO	Bioassay								
	Sediment	2 <W	2 <W	1 <W	1 <W	1 <W	2 <T	1 <W	1 <W
	Field								
Stn 134 – 15	Sediment	2 <W	2 <W	1 <W	1 <W	1 <W	1 <W	1 <W	1 <W
	(Range)	(<W)	(<W)	(<W)	(<W)	(<W)	(<W)	(<W)	(<W)
Upstream of Polysar 66" and 72" sewers	Bioassay								
	Sediment	2 <W	8 <T	1 <W	1 <W	1 <W	15	134	135
	Field								
Stn 47 –35	Sediment	10 <T	29	2 <T	4 <T	9 <T	21	127	142
	(Range)	(<T)	(23–35)	(<W–<T)	(<T)	(<T–11)	(19–22)	(100–171)	(97–184)
Downstream of Polysar 66" and 72" sewers	Bioassay								
	Sediment	2 <W	6 <T	1 <W	1 <W	1 <W	85	990	210
	Field								
	Sediment	658	164	110	33	205	339	5149	473
Stn 74 –20	(Range)	(558–750)	(150–176)	(54–216)	(31–36)	(136–323)	(249–510)	(1712–6880)	(312–737)
50 m downstream of Dow 1st Street sewer	Bioassay								
	Sediment	2 <W	130	200	1 <W	230	2900	45000	1500
	Field								
	Sediment	952	366	184	541	471	1044	7473	482
Stn 95 –34	(Range)	(440–1684)	(208–601)	(114–260)	(338–925)	(268–725)	(733–1603)	(6650–8810)	(432–540)

Shading indicate sediment trace metal concentrations that exceed PSQG–SELs.

NA – Not Available; <W – Not Detected; <T –Trace Amount.

For the upstream reference station, the frequency of non-detectable and trace levels were similar for laboratory and field samples. Hexachlorobutadiene was found in measurable amounts in both sets of samples. The station with intermediate organic chemical concentrations (Stn 47-35) showed fairly close agreement between the bioassay and field sediments. The largest discrepancies began to appear at the more contaminated sites (Stns 74-20 and 95-34). Several organic chemicals that were measured in the field samples were not retained in the laboratory sediments and were only reported at non-detectable or trace amounts. These compounds included HCE, 1,2,4-tCB and 1,2,3,5-teCB. The less chlorinated benzene compounds have a higher volatility rate as compared to those more chlorinated. These losses from volatilization would have occurred while the sample was in contact with air, such as during sieving and homogenization. Several other compounds were also reported at lower concentrations in the laboratory samples for Stn 74-20 and appear to be outside the concentration range observed in the field. For Stn 95-34 sediment, the reverse occurred and substantial increases in concentration for those compounds that have a greater affinity for sediments were noted for the laboratory samples as compared to the range of concentrations encountered in the field. Sediment concentrations were 177% higher for QCB, 502% higher for HCB and 211% higher for OCS, suggesting possible cross-contamination of a small pocket of extremely contaminated sediment. Some of the highest HCB and OCS sediment concentrations were found at transect 95 (Table 6). Concentrations approach those levels associated with "puddles" often found on or just below the sediment surface (Kauss, 1996).

Loss of contaminants, as high as 100% in some cases, from the sediment before testing will underestimate potential exposure concentrations under field conditions, particulary for compounds with high volatility. On the other hand, sediments collected from more contaminated areas may be subjected to increased contaminant levels of the more prevalent compounds. The implication of these differences will be discussed during the interpretation of the toxicity data.

3.3 Mayfly (*Hexagenia limbata*) 21-day Lethality and Growth Results

The biological data for the two endpoints, mortality and growth, are summarized in Tables 7, 7A and 7B. Statistical analysis was omitted for the spring 1994 data set, given the lack of sample replication in the laboratory. Relative differences in lethality are described among sites. Both the control and reference control mortality were well below the acceptable criterion of 15% mortality. Percent mortality was highly variable among transects and ranged from 0% to 100%. This trend was also evident among sites along a particular transect, suggesting a high degree of localized impact. Of the 36 test sediments, 33% were highly toxic with reported percent mortality above 50% (Figure 2). Survival was lowest (100 % mortality) at Stns 73-30, 136-10, 45-35, 48-37 and 49-40, which tended to coincide with those locations furthest from the shore. Prior to death, several of these test sediments (Stns 73-30, 136-10, 45-35 and 95-37), initially produced an immediate avoidance response by the test animals. By Day-3, at least 50% of the animals were found dead for Stns 136-10 and 95-37 and the presence of nymphs on the sediment surface continued at Stns 45-30 and 73-30 for several days. Other stations along transects 45 (downstream of Cole Drain) and 73 (downstream of ESSO) resulted in delayed avoidance behaviour.

TABLE 7. Summary of biological results on mayfly, midge and minnow sediment bioassays for control(s) and St. Clair River 1994 sediments. Mean values (± standard deviation).

Test Organism		*Hexagenia limbata* (Mayfly)		*Chironomus tentans* (Midge)		*P. promelas* (Fathead Minnow)
Transect	*Station Number* (m offshore)	*% Mortality* (N=1)	*Ave. Individual Body Weight* (mg wet wt.)	*% Mortality* (N=1)	*Ave. Individual Body Weight* (mg wet wt.)	*% Mortality* (N=1)
Control		0	8.25 (3.6)	27	6.64 (3.1)	0
		0	9.69 (4.1)	0	6.69 (2.3)	10
		0	7.57 (4.4)	0	6.10 (3.0)	0
Reference	134 – 15	0	27.25 (11.0)	0	10.40 (2.6)	0
Upstream of ESSO	–25	10	7.64 (5.0)	7	4.83 (2.7)	0
	–35	0	20.82 (10.3)	7	6.31 (3.0)	10
Downstream of	44 – 15	0	11.62 (4.9)	7	8.90 (2.4)	100
ESSO intake above	–30	60	7.10 (1.8)	60	1.03 (0.9) *	100
discharge	–45	80	–	100	–	0
Upstream of	73 – 10	40	6.87 (2.7) *	0	2.48 (1.7) *	0
Cole Drain	–20	0	6.84 (4.0) *	93	–	10
	–30	100	–	100	–	20
Downstream of	136 – 10	100	–	100	–	100
Cole Drain	–20	0	16.01 (6.1)	20	6.25 (2.9)	20
discharge	–30	90	–	93	–	60
Upstream of Polysar	45 – 5	10	7.23 (3.4) *	0	8.26 (2.1)	0
54" sewer	–20	0	8.56 (3.8)	0	2.78 (0.6) *	10
	–35	100	–	100	–	20
95 m downsteam of	46 –7	0	18.98 (6.6)	7	9.24 (2.6)	20
Polysar 54" sewer	–15	0	11.79 (5.3)	7	6.34 (2.8)	10
	–25	40	7.24 (4.9)	87	–	10
200 m downstream	94 – 10	10	14.98 (3.8)	0	8.77 (2.4)	80
of Polysar 54" sewer	–25	0	28.47 (9.1)	0	7.27 (2.3)	100
	–40	0	11.51 (5.0)	0	8.04 (2.6)	0
Upstream of Polysar	47 – 15	70	–	27	1.14 (0.9) *	0
66" and 72" sewers	–35	10	13.55 (7.2)	20	4.52 (1.9)	90
	–55	0	18.33 (7.3)	13	7.61 (3.4)	0
Downstream of	74 – 5	0	7.85 (2.6)	0	9.73 (3.2)	80
Polysar 66" and 72"	–20	10	18.75 (5.7)	13	7.78 (2.6)	100
sewers	–30	80	–	47	1.28 (0.7) *	0
50 m downstream	95 – 10	10	8.91 (3.1)	0	10.56 (3.0)	30
of Dow 1st Street	–30	0	29.25 (16.7)	7	8.93 (2.1)	100
sewer	–37	80	–	100	–	60
Downstream of	48 – 10	0	23.29 (8.0)	13	8.15 (2.0)	100
Dow 1st Street	–25	0	22.82 (8.5)	0	8.63 (2.6)	10
sewer	–37	100	–	33	3.64 (2.7) *	20
Downstream of	49 – 10	0	19.29 (6.5)	0	8.70 (2.0)	40
Dow 1st Street	–25	30	6.83 (2.0) *	7	4.92 (1.5)	30
sewer	–40	100	–	33	8.12 (3.8)	100
Downstream of	96 – 22	10	27.34 (14.4)	0	9.53 (2.3)	10
Dow 2nd Street	–28	10	9.00 (3.6)	7	6.38 (3.7)	0
sewer	–35	50	6.01 (1.1) *	0	3.36 (1.5) *	0

* Body weight significantly lower than the average reference control sediment (LSMEANS; $p<0.02$).

TABLE 7A. Summary of biological results on mayfly and midge QA sediment bioassays for control and fall 1994 St. Clair River sediments. Mean values (± stand. deviation).

Test Organism		*Hexagenia limbata* (Mayfly)		*Chironomus tentans* (Midge)	
Transect	*Station Number* (m offshore)	*% Mortality* (N=3)	*Ave. Individual Body Weight* (mg wet wt.)	*% Mortality* (N=3)	*Ave. Individual Body Weight* (mg wet wt.)
Control		A 0 (0)	8.85 (0.8)	A 8.8 (4)	12.46 (0.1)
Polysar Downstream of Cole Drain	136 – 10	D * 100 (0)	–	B * 100 (0)	–
	136 – 20	A 0 (0)	7.68 (0.5)	A 2.2 (4)	12.21 (4.0)
	136 – 30	D * 96.6 (6)	–	B * 100 (0)	–
Dow Downstream of 1st St. sewer	95 – 10	B * 16.6 (6)	4.58 (0.7)	A 6.6 (7)	14.23 (3.4)
	95 – 30	C * 86.6 (6)	–	A 11.0 (4)	16.30 (1.9)
	95 – 37	D * 100 (0)	–	B * 97.7 (4)	–
Mean		57.1	7.03	46.6	13.80
Standard Deviation		2.4	0.67	3.1	2.37
% Minimum Significant Difference		7.8	–	7.8	–
% C.V		4.2	9.5	6.6	17.1
Discriminatory Power		41.6	4.6	31.6	1.7

* % Mortality value is significantly different than the control sediment (Dunnett't one–tailed t–test; $p<0.05$).

TABLE 7B. Summary of biological results on mayfly, midge and minnow sediment bioassays for control(s) and upper St. Clair River 1995 sediments. Mean values (± stand. deviation).

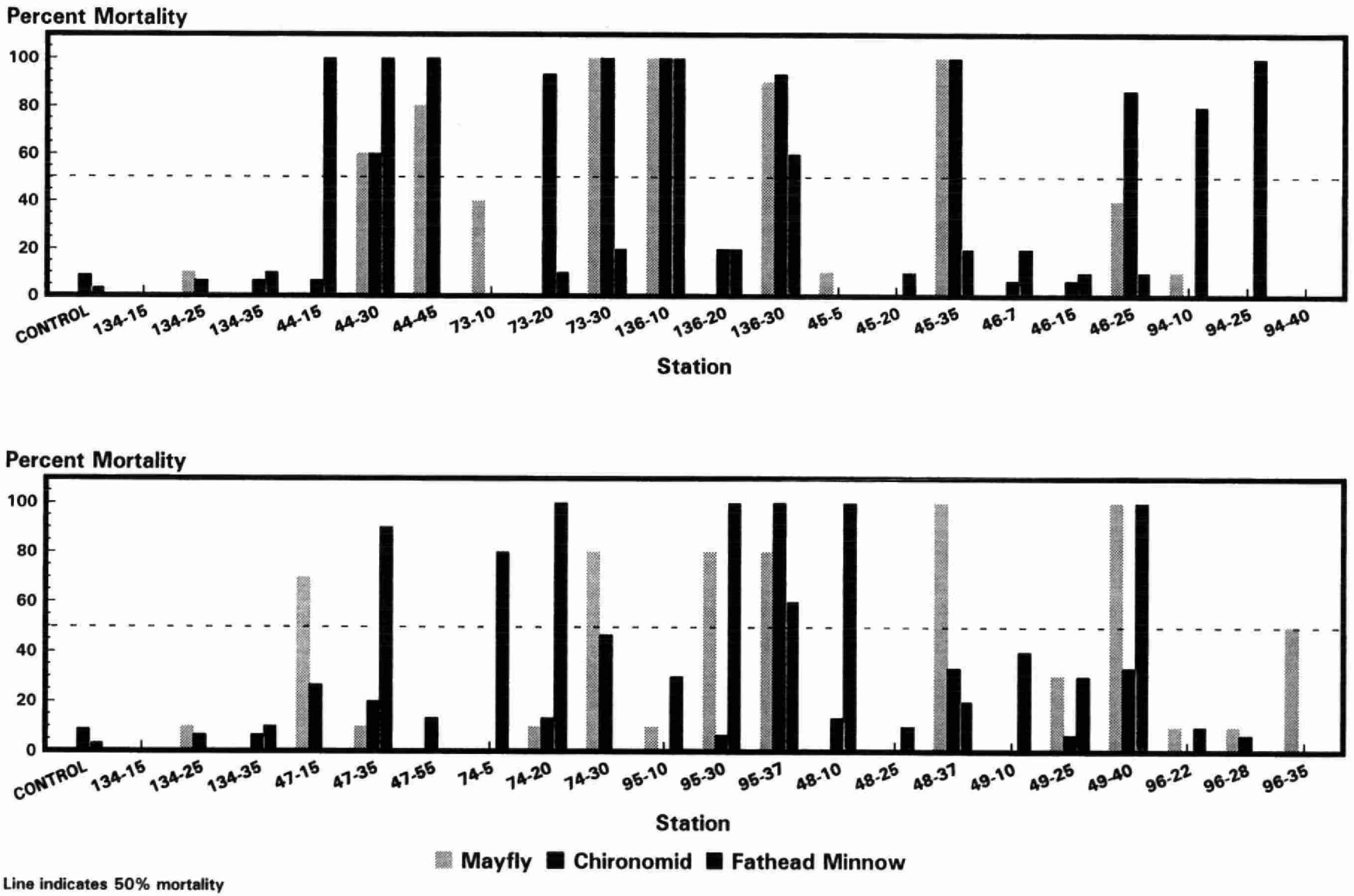
Test Organism		*Hexagenia limbata* (Mayfly)		*Chironomus tentans* (Midge)		*P. promelas* (Fathead Minnow)
Transect	*Station Number* (m offshore)	*% Mortality* (N=3)	*Ave. Individual Body Weight* (mg wet wt.)	*% Mortality* (N=3)	*Ave. Individual Body Weight* (mg wet wt.)	*% Mortality* (N=3)
Control		A 0 (0)	C 7.34 (1.4)	AB 15.5 (4)	B 9.71 (0.2)	A 3.3 (6)
Reference Upstream of ESSO	134 – 15	A 0 (0)	B 26.52 (2.0)	A 6.6 (7)	A 12.66 (1.1)	B** 100 (0)
Polysar Upstream of 66" sewer	47 – 35 Replicate 1	A 0 (0)	B 27.93 (11.3)	A 2.2 (4)	B 9.61 (1.6)	B** 100 (0)
	47 – 35 Replicate 2	A 0 (0)	A 35.56 (1.4)	A 6.6 (7)	B 9.59 (0.3)	B** 93.3 (12)
Polysar Downstream of 72" sewer	74 – 20	A 0 (0)	B 27.82 (2.8)	A 2.2 (4)	B 9.80 (0.9)	AB** 66.6 (58)
Dow Downstream of 1st St. sewer	95 – 34	B* 100 (0)	--	B* 64.4 (45)	--	B** 100 (0)
Mean		20.0	29.4	16.4	10.4	91.9
Standard Deviation		0.0	4.3	13.4	0.9	14.0
% Min. Significant Difference		39.0	–	50.2	–	–
% C.V.		0.0	14.6	81.7	8.8	15.2
Discriminatory Power		–	2.0	4.6	3.4	2.3

* % Mortality value is significantly different than the control and reference sediment (Dunnett's 1–tailed t–test; $p<0.05$).

** % Mortality value is significantly different than the control sediment only (Dunnett's 1–tailed t–test; $p<0.05$).

A Means sharing a common letter within a column are not significantly different; Tukey's HSD test for % Mortality ($p<0.05$) and planned comparisons using LSMEANS for comparing Body Weight ($p<0.01$).

FIGURE 2. Organism Mortality for St. Clair River 1994 Sediments



Line indicates 50% mortality

Growth data between each test site and the average growth measured for the reference location (transect 134) was compared using LSMEANS. The level of significance would be a conservative estimate of significant difference because the variability in the test sediments is based on within-jar rather than among-jar variability. Growth reduction was found at only five stations, where there were sufficient number of surviving animals (Figure 3).

Of the six stations tested in spring 1994 and repeated in the fall, virtually identical results were found (Table 7A). The three stations (Stn 136-10, 136-30, 95-37) found to be toxic in the spring (>80% mortality) were also extremely lethal in the fall (>96% mortality). The only anomaly occurred for Stn 95-30, where the toxicity dramatically increased from 0% to 86% mortality. Time to death observations indicated an acute lethal effect for Stns 136-10 and 95-37, where at least an average of 80% of the test organisms died by Day-4. As for the balance of the mayflies, there were notable differences between stations. At Stn 95-37, the remaining survivors displayed sporadic gill movement just above the sediment surface while at Stn 136-10, animals appeared to be actively burrowing. The first signs of animal departure from the burrows from Stns 95-10 and 95-30 did not take place until eight days into the test.

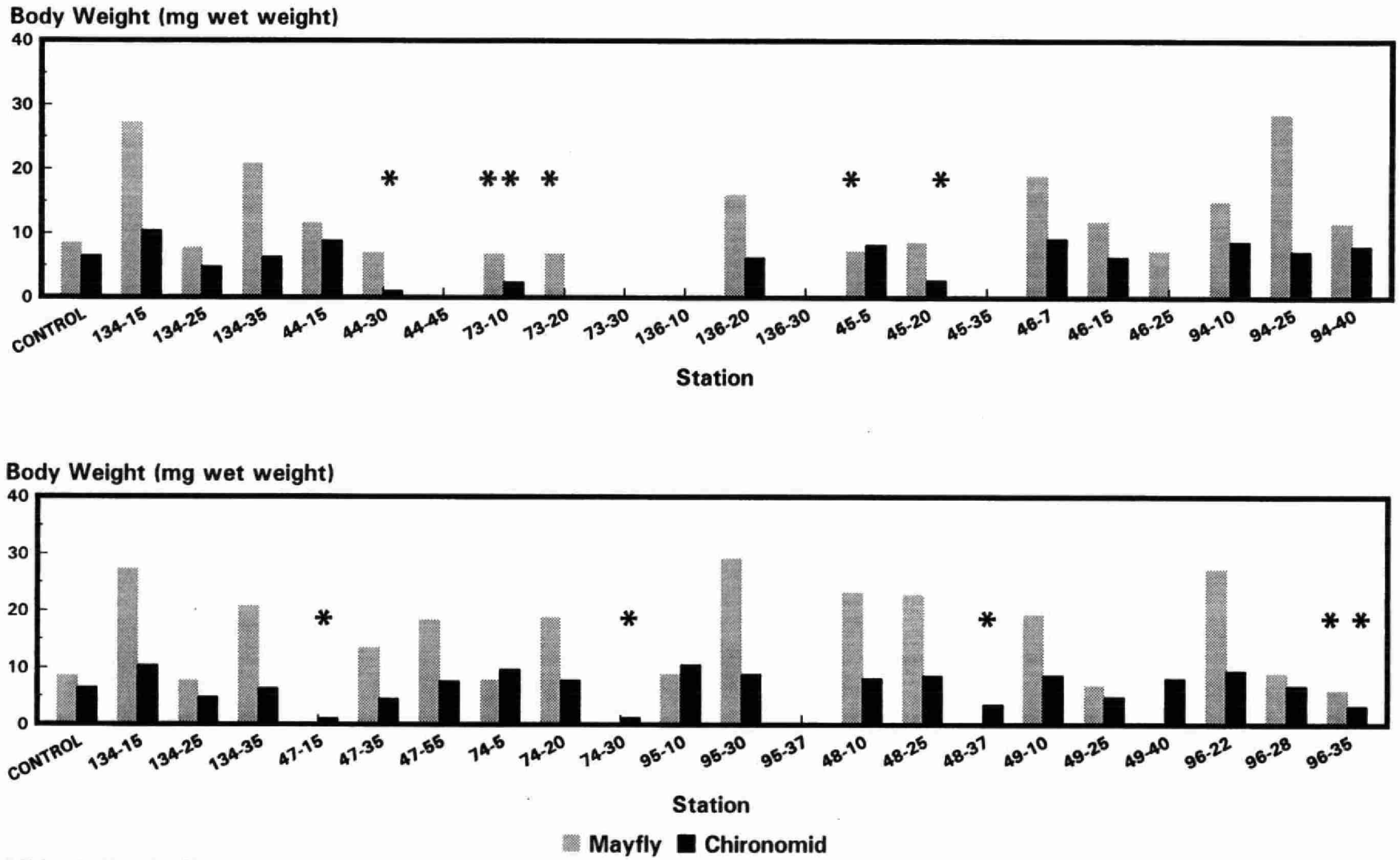
For the spring 1995 study, mayfly mortality was nil for three of the test sediments and both control sediments (Table 7B). Mortality was 100% for mayfly larvae exposed to 95-34 sediment and differed significantly relative to the control and other test sediments ($p<0.0001$). Laboratory inspection of the test chambers showed Stn 95-34 sediment was acutely toxic, no survivors were found after Day-6. A strong avoidance behaviour was evident by Day-3, the mayfly nymphs were either deceased or found on the sediment surface rather than burrowing normally.

Significant differences in the sublethal growth endpoint was measured among sites ($p<0.0001$). This occurred only for the control animals, which had the lowest average individual body weight (7.3 mg, wet weight). Comparison analyses indicated a similar range of growth for each of the test sediments (26.5 to 35.5 mg). Growth at these locations resulted in at least a five-fold increase in biomass relative to the average mayfly starting size. The lower mayfly growth obtained for the control sediment was probably due to the quality and quantity of the nutritional value associated with the sediment due to the prolonged storage of this sediment, relative to the fresh detrital material found in the reference and test sediments.

3.4 Chironomid (*Chironomus tentans*) 10-day Lethality and Growth Results

Results for chironomid growth and lethality are reported in Tables 7, 7A and 7B. A cursory examination of midge survival among sites for the spring 1994 study will be discussed due to the restriction on statistical replication. Chironomid survival in both controls averaged less than the acceptable control mortality of 25%. Midge mortality was highly variable among and between transects. Values ranged from 0% to 100% mortality. At least 25% of the sites were acutely toxic (>50% mortality) and 8% moderately toxic (33% to 50% mortality). Four stations resulted in 100% lethality, Stns 44-45, 73-30, 136-10, 45-35 and 95-37, which mostly represented sediments collected furthest from shore.

FIGURE 3. Mayfly and Midge Growth for St. Clair River 1994 Sediments



* Value significantly different than the reference control (134-15 or -25 or -35).
Growth not shown for sites with >70% mortality.

C. tentans exposed to Stns 44-30, 73-10, 45-20, 47-15, 74-30, 48-37 and 96-35, which had sufficient number of surviving midges, resulted in a lower growth capacity relative to the control animals ($p<0.0001$) (Figure 2). This translated into at least a 31% reduction in fresh body weight.

The grouping of lethal and non-lethal sediments in the fall 1994 survey agreed well with those found in the spring toxicity test (Table 7A). Sediment from 136-10, 136-30 and 95-37 were found to be acutely toxic, with greater than 97% mortality. The remaining test sediments resulted in a similar degree of effect as the control exposure (Range: 2% to 11% mortality).

Results for spring 1995 chironomid growth and lethality are reported in Table 7B. Percent mortality for the midge ranged from 2% to 64% The only significant increase in mortality occurred for Stn 95-34, as compared to the reference control mortality of 6% and the negative control mortality of 15% (Dunnett's one-tailed *t*-test, $p<0.05$). Variable toxicity was reported among replicates but did not alter this ranking. *Chironomus* growth fell within a similar range for the control and test sediments and was notably different than the reference control animals (12.6 mg) ($p<0.0003$).

3.5 Fathead Minnow (*Pimephales promelas*) 21-day Lethality Results

Juvenile fathead minnow percent mortality data is reported in Tables 7 and 7B, for the spring 1994 and 1995 studies, respectively. In 1994, sufficient control survival was attained for both the control and reference control exposures ($\leq$ 10% mortality)(Table 7). Toxicity values varied extensively among locations based only on single determinations per station. At least one-third of the stations resulted in a high degree of mortality ($\geq$ 60% mortality) and minimal organism loss was noted for at least one-half of the stations ($\leq$ 20% mortality). Several of the sites reporting high lethality were limited to the nearshore and mid-point. The minnow toxicity tests were completed at two different time intervals, the first batch of tests consisting of 18 randomly selected test sediments and the second set of sediments consisted of the remaining 18 test sediments. The first set of bioassays was completed in August-September 1994, along with the midge and mayfly assays, while the other test was completed in September-October 1994. Overall, the difference in storage time of the sediments did not appear to bias the minnow toxicity results. The ratio of highly toxic ($\geq$ 60% mortality) to moderate and non-toxic ($<$ 60% mortality) samples in Phase I and Phase II were 5:13 and 7:11, respectively.

Daily records of number of mortalities for the eight stations that resulted in 100% lethality indicated that for the majority of these sediments, loss of fathead minnows commenced on Day-10 thru Day-15. The fastest rate of death was noted for Stns 44-15, 44-30, 94-25, 74-20, 48-10 and 49-40, where all of the animals died within a four day time span.

In the spring 1995 toxicity tests, minnow survival was greatly reduced for animals exposed to the reference control, Stn 47-35 and 95-34 sediments (Table 7B). Percent mortality exceeded 93% at these locations. Moderate level of mortality was reported for Stn

74-20 (66%) but was not significantly higher than the control sediment. Control mortality indicated acceptable conditions during the 21-day test for the negative control only. Death did not commence until Day-13, at which time at least 53% of the fish were dead for Stn 74-20. In fact, loss of minnows for Stn 74-20 only occurred over a two day period and no additional losses were noted after Day-14. Minnows exposed to Stn 47-35 and 134-15 sediments gradually died over a six day period (Day-13 thru Day-18). Fifty percent of the animals were dead by Day-15. Delayed toxicity was observed for the Stn 95-34 exposures, with the majority of deaths falling within the last three days of the test.

3.6 Quality Assurance Toxicity Tests

Replicated Sediment Toxicity Test

The results of the fall 1994 sediment toxicity test were used to evaluate the repeatability of the test data, in conjunction with examining any temporal variability in toxicity. The toxicity data provided an estimate of intralaboratory test precision, which was lacking in the experimental design used in the spring 1994 toxicity tests. This was owing to the incapacity of replicating each of the 39 individual samples. Of the original 13 transects, benthic invertebrate sediment toxicity tests were completed for two transects in fall 1994. Enough sediment was obtained at each of the three sampling points along each transect to complete the tests using three laboratory replicates per sample. This sampling design provided an opportunity to measure within sample variability. Unfortunately, a similar analysis was not completed for the fathead minnow 21-day toxicity test.

Coefficient of variation was calculated for each endpoint and showed excellent test precision (Range: 4 % to 17% C.V.) across species and test response (Table 7A). The lower the C.V., the greater the confidence in the precision or accuracy of the test results. Another useful quantitative measure of test precision is the minimum significant difference or MSD, which describes the ability to detect a significant effect in the paired response between the control versus the test sample. The MSD was determined for percent mortality and at 8% was found to be identical for both benthic species. In other words, a mean mortality value as small as 16% for a test sample would be deemed a significant toxic response given a mean control mortality of 8%, as was the case for the midge assay. Other reported MSDs for *C. tentans* 10-day sediment lethality tests include MSD = 38% (Becker *et al.*, 1995) and MSD = 14% (Burton *et al.*, 1996). The latter value is based on interlaboratory performance which tends to be higher than that calculated for intralaboratory studies, as was the case in this report. The mortality endpoint yielded the best discriminatory power values (D.P. 31 and 41), relative to the growth endpoint (D.P. 1 and 4). The ability to distinguish between lethal and non-lethal sediment samples was in part due to the small variability among replicates and is a reflection of the broad range in response which varied between 0%-2% to 100% mortality for both the mayfly and midge. Substantially lower D.P. was noted for growth because of the limited number of samples capable of yielding a suitable growth measurement.

A similar analysis of the data generated for the 1995 toxicity tests revealed a quite different group of estimates (Table 7B). Generally, the test sediments were chosen from less toxic sites, with the exception of Stn 95-34. The lack of sediments of intermediate toxicity

caused the response range to be rather narrow (all or none response) and this affected the D.P. of the assays which were fairly low (D.P.: 2 to 4) and the MSD for lethality to be higher (39% and 50%). The midge and mayfly toxicity tests both were capable of ranking the test sediments in a consistent manner and had reasonable test precision (Range: 0% to 82% C.V.).

Reference Toxicity Tests

The 48-hour copper LC50s (95% C.I.) for the water-only reference toxicant exposures for *H. limbata* for the spring 1994, fall 1994 and 1995 studies were 0.97 (0.60 - 1.88) mg/L; 1.01 (0.62 - 2.06) mg/L; and 1.68 (0.98 - 4.23) mg/L, respectively. These values were within their respective acceptable 48-h LC50 (± 2 s.d.) range of 0.93 (0.11) mg/L; 1.02 (0.22) mg/L; and 1.02 (0.19) mg/L, according to a previous series of reference toxicant tests.

Similarly, for *C. tentans*, the LC50s were 1.31 (1.12 - 1.56) mg/L; 1.28 (0.66 - 4.81) mg/L; and 1.13 (0.94 - 1.40) mg/L, as compared to an expected 48-h LC50 (± 2 s.d.) of 1.59 (0.79) mg/L; 1.61 (1.13) mg/L; and 1.55 (1.02) mg/L, for the spring 1994, fall 1994 and 1995 tests, accordingly.

3.7 Chemical Bioaccumulation in *Pimephales promelas*

The examination of organic chemical availability to aquatic organisms is valuable for assessing the potential for chemical transfer through the food web. The primary objective of this test procedure is to make general observations on whole organism tissue concentrations as they relate to overall bulk organic chemical concentrations in the sediment and differences in chemical uptake among transects. Surviving fathead minnows were submitted for pesticide, total PAHs, total PCBs and several chlorinated organics and are based on whole-body tissue concentrations (ng/g, dry weight). A dry to wet ratio of 0.16 was used to convert from a wet weight to a dry weight basis.

The sources of organic compound accumulation to forage fish include direct contact with the sediment and uptake from the overlying water. Factors that control chemical accumulation by forage fish include those that affect chemical adsorption and desorption such as sediment organic content, particle size distribution and chemical partition coefficient, also known as the octanol-water partition coefficient, Kow (Lake *et al.*, 1990). Biotic factors affecting uptake include metabolism and lipid content (Boese *et al.*, 1995).

Table 8 summarizes those chemicals that were measured at or above trace concentrations (dry weight) in surviving juvenile fathead minnows from the spring 1994 sediment toxicity test. Whole-organism chemical concentrations are based on duplicate samples for the control only. Insufficient biomass was obtained from each station, necessitating the pooling of surviving animals across a transect; thereby the degree of variability in uptake is unknown and statistical comparisons were not feasible. Despite the small sample size, casual observations of chemical tissue concentrations among transects were possible.

TABLE 8. Select organic concentrations (ng/g, dry weight) in fathead minnows exposed to control and St. Clair River 1994 sediments in the laboratory.

Sample size n = 1, except for the control n = 2.

	Transect	pp–DDE	Total PCBs	Hexachloro–butadiene	Pentachloro–benzene	Hexachloro–benzene	Octachloro–styrene
Control		62	125 <W	18	6 <W	18 <T	6 <W
Reference Upstream of ESSO	134	37 <T	1256	56	25 <T	879	276
Downstream of ESSO intake above	44	44 <T	125 <W	18	6 <W	12 <T	6 <W
Upstream of Cole Drain	73	75	125 <W	18	6 <W	56 <T	37 <T
Downstream of Cole Drain outtake	136	81	125 <W	44	25 <T	690	2763
Upstream of Polysar 54" sewer	45	62	1004	37	6 <W	414	3391
95 m downsteam of Polysar 54" sewer	46	18 <T	1507	37	6 <W	816	7536
200 m downstream of Polysar 54" sewer	94	56	125 <W	69	6 <W	370	753
Upstream of Polysar 66" and 72" sewers	47	37 <T	502	25	6 <W	420	3202
Downstream of Poly. 66 & 72" sewers	74	81	1004	251	100	5526	2700
50 m downstream of Dow 1st St. sewer	95	6 <W	3642	10676	1256	36424	6217
Downstream of Dow 1st Street sewer	48	18 <T	4270	3202	879	33284	16956
Downstream of Dow 1st Street sewer	49	69	6908	94	131	11932	2888
Downstream of Dow 2nd Street sewer	96	37 <T	2260	125	88	3391	942

< W – Not Detected; < T – Trace Amount.

Minnow tissue concentrations calculated using a dry to wet weight ratio of 0.16.

The majority of the chemicals selected for analyses were not detected in the minnows for all test and control sites e.g. 16 PAHs, heptachlor, aldrin, mirex, pp-DDD, pp-DDT, HCE, tCBs, tCTs, and teCBs. Six compounds were routinely measured above trace amounts and included pp-DDE, total PCBs, HCBD, QCB, HCB and OCS, in the test minnows. Several field studies measuring body burdens for organic compounds in endemic biota which focused on the St. Clair River and Lake St. Clair have routinely found detectable concentrations for those organochlorines of higher Kow (OMOE, 1991; Pugsley *et al.*, 1985; Gobas *et al.*, 1989; Suns *et al.*, 1991). The Kow is a parameter describing the lipophicity or hydrophobicity of a chemical. In other words, the greater the Kow, the greater the likelihood of the chemical accumulating in organisms, primarily the lipid portion (Mackay, 1982). The range in log Kow for HCBD, QCB, HCB and OCS is from 4.80 to 6.29. The other less chlorinated compounds, tCBs and teCBs, have substantially lower Kows ranging from 3.98 to 4.51 and did not result in any bioaccumulation by fathead minnows under identical test conditions.

In this study, the distribution of pp-DDE was fairly uniform among control and test sites suggesting a certain degree of background contamination. This trend also occurred for HCBD, except for the two elevated concentrations reported for transects 95 and 48. Minnow tissue concentrations for total PCBs, HCB and QCB followed a distinct distribution pattern, where proportionately higher tissue concentrations were reported for transects below the Dow 1st street discharge (transects 95, 48, 49 and 96). On average, tissue concentrations were 3.3 times higher for PCB and 23.5 times higher for QCB, as compared to the animals exposed to the reference or transects situated furthest upstream. The highest tissue concentrations were reported for HCB at three of the Dow transects (Range: 11932 to 36424 ng/g), where concentrations were at least 13.5 times higher than the reference control minnows. Octachlorosytrene tissue concentrations exhibited a widespread occurrence of elevated tissue concentrations (Range: 753 to 16956 ng/g, n = 10 transects). Only the control, reference and transect 44 and 73 samples resulted in lower concentrations. These trends in organic chemical distribution in fathead minnows has been also reported in sediment bioaccumulation tests conducted in 1990 (Bedard and Petro, 1992a).

Usually, concentration factors are calculated to assess the relative availability of each organic compound for the test and control sediments. The biota-sediment accumulation factor or BSAF is defined as the ratio of organic chemical concentration in the fathead minnow, normalized for percent lipid, to that in the bulk sediment after correction for organic content (Lake *et al.*, 1990, Ankley *et al.*, 1992). However, the need to pool surviving animals across a transect, in addition with the unequal survival among sites along a transect, made it difficult to accurately determine the level of chemical exposure (Cs), according to the following equation;

$$BSAF = (C_t / L) / (C_s / TOC)$$

where,

C_t = tissue contaminant concentration (ng/g tissue, dry weight)
L = tissue lipid concentration (g/g tissue)
C_s = sediment contaminant concentration (ng/g sediment, dry weight)
TOC = total organic carbon content of sediment (g/g sediment)

Despite the limitations in calculating exact BSAFs, a few comments can be made regarding those sites not affected by high mortality (transects 45, 46 and 96). Among these

three transects, HCB and OCS appear to be more available for uptake and the ratio between organism and sediment concentrations (uncorrected values) was higher than 1.0. In other words, average whole organism chemical concentrations surpassed those measured in the sediment. At transect 46, the BSAF (uncorrected) for HCB was 8.1 and 12.9 for OCS. Octachlorostyrene tissue concentrations appear to exceed levels associated with the sediment, suggesting chemical bioaccumulation. Elevated OCS in biota have been attributed to both the high Kow and the slower rate of depuration of the chemical from the organism, thereby resulting in increasing concentrations in the organism with time (Oliver, 1987; Oliver and Niimi, 1983).

In the 1995 sediment toxicity test, difficulty arose in acquiring enough biomass for chemical analyses for the reference control and test exposures. This was a result of the acute toxic effect of the sediments which provided few surviving minnows after 21 days. Therefore, an assessment on the relative availability of contaminants to fish was not completed.

4.0 DISCUSSION

Spatial Trends in Sediment Toxicity

The first series of toxicity tests consisted of 36 test sites, with three sites for each of the 12 transects, three reference control sites collected along a single transect and a negative control sediment. The spring 1994 survey identified a number of potentially toxic sediments throughout the designated study area through the use of a battery of sediment toxicity tests. Each test sediment was ranked by varying degrees using the following categories (listed from least impacted (high quality) to most impacted (very low quality)): non-impacted (high), slightly impacted (slight), intermediately impacted (moderate), strongly impacted (low) and very strongly impacted sites (very low) (Table 9). The ranking is based on the number of positive hits for each of the five biological endpoints, with a heavier weighting placed on the lethal response. Each endpoint received either a toxic (T) or non-toxic (N) rating depending on whether the effect was considered significantly different relative to the reference and/or control responses. Since the spring 1994 toxicity tests were completed on unreplicated samples, either the MSD value observed in the fall 1994 toxicity tests or a default value representing the required acceptable control mortality criteria was used in the assessment of the spring 1994 toxicity data.

According to the first approach, which refers to the fall 1994 benthic toxicity tests, a MSD of 8% was derived for the *Hexagenia* and *Chironomus* lethality response. Application of this MSD for the spring 1994 data set resulted in 15 hits for both mayfly and midge survival. Alternatively, using a more conservative estimate of whether an effect was significant would be determined by comparing the percent mortality value against the control mortality criterion of 15% mortality for mayfly and minnow results and 25% for the midge test. Under this scenario, 15, 13 and 16 hits were detected for mayfly, midge and minnow survival, respectively. The growth results were compared statistically to the reference control data based on the level of within-jar variation. This would underestimate the level of significance, as compared to using a measure of between-jar variance. Limited information regarding growth effects was available in the fall 1994 quality assurance study and emphasis

TABLE 9. Spatial variability in sediment toxicity and sediment quality for St. Clair River spring 1994 samples.

Transect	Station Number (m offshore)	Sediment Quality	Mayfly Mortality	Mayfly Ave. wet wt.	Midge Mortality	Midge Ave. wet wt.	Minnow Mortality
Reference	134 – 15	High	N	N	N	N	N
Upstream of ESSO	–25	High	N	N	N	N	N
	–35	High	N	N	N	N	N
Downstream of	44 – 15	Moderate	N	N	N	N	T
ESSO intake above	–30	Very Low	T	N	T	T	T
discharge	–45	Low	T	–	T	–	N
Upstream of	73 – 10	Slight	N	T	N	T	N
Cole Drain	–20	Moderate	N	T	T	–	N
	–30	Low	T	–	T	–	N
Downstream of	136 – 10	Very Low	T	–	T	–	T
Cole Drain	–20	High	N	N	N	T	N
discharge	–30	Very Low	T	–	T	–	T
Upstream of Polysar	45 – 5	High	N	T	N	N	N
54" sewer	–20	High	N	N	N	T	N
	–35	Low	T	–	T	–	N
95 m downsteam of	46 –7	High	N	N	N	N	N
Polysar 54" sewer	–15	High	N	N	N	N	N
	–25	Slight	N	N	T	–	N
200 m downstream	94 – 10	Slight	N	N	N	N	T
of Polysar 54" sewer	–25	Moderate	N	N	N	N	T
	–40	High	N	N	N	N	N
Upstream of Polysar	47 – 15	Moderate	T	–	N	T	N
66" and 72" sewers	–35	Moderate	N	N	N	N	T
	–55	High	N	N	N	N	N
Downstream of	74 – 5	Slight	N	N	N	N	T
Polysar 66" and 72"	–20	Moderate	N	N	N	N	T
sewers	–30	Low	T	–	N	T	N
50 m downstream	95 – 10	High	N	N	N	N	N
of Dow 1st Street	–30	Moderate	N	N	N	N	T
sewer	–37	Very Low	T	–	T	–	T
Downstream of	48 – 10	Moderate	N	N	N	N	T
Dow 1st Street	–25	High	N	N	N	N	N
sewer	–37	Moderate	T	–	N	T	N
Downstream of	49 – 10	High	N	N	N	N	N
Dow 1st Street	–25	High	N	T	N	N	N
sewer	–40	Low	T	–	N	N	T
Downstream of	96 – 22	High	N	N	N	N	N
Dow 2nd Street	–28	High	N	N	N	N	N
sewer	–35	Moderate	T	T	N	T	N

N – Not Toxic; T – Toxic.

will be placed on lethal effects when describing the toxicity results.

A large number of the sites were highly toxic ($\geq$ 70% mortality) or moderately toxic ($\geq$ 40% and < 70% mortality), to at least one of the test species. Four of the stations were deemed extremely toxic due to the high mortality experienced by all three test organisms. These sites were located downstream of industrial discharge points that included one site collected downstream of the ESSO intake (Stn 44-30), two stations situated downstream of the Cole Drain (Stn 136-10 and 136-30) and a single site downstream of Dow 1st street sewer (Stn 95-37). At least 7% of the total number of sites were identified as being highly toxic and 7% moderately toxic using the mayfly and midge assays only. These sites targeted each of the industrial zones. Listing the sites from upstream to downstream are ESSO (Stn 44-45 and 73-30), Cole Drain (Stn 45-35), Polysar (Stn 46-25 and 74-30) and Dow (Stn 48-37). All of the sites were located the furthest distance from shore for the respective transects but still restricted to the nearshore region of the river (< 45 metres), while sites which were less than 20 m offshore continually showed little or no toxic effect on the same test species. Conversely, none of these sites produced high fish mortality, indicating poor concordance between the bottom-dwelling and pelagic species. Overall, minnow lethality was not significantly correlated with either mayfly or midge survival and growth (Table 10). Sites that were toxic to fish varied widely throughout the study area, as was the case for the benthic toxicity tests, but at completely different stations. There was a strong correspondence between lethal and sublethal effects for the two benthic species for the entire study area ($r = +0.60$ to 0.83, $p < 0.001$ to 0.0001) (Table 10).

Temporal Variability in Sediment Toxicity

Temporal differences in sediment toxicity both seasonally and annually showed excellent concordance. In most cases, sediments identified as being either highly toxic or non-lethal in spring 1994 remained that way in the fall when the sediments were re-sampled (Figure 4). The only anomaly observed was the significant effect on mayfly survival which was absent in the spring for Stn 95-30. Similarities along a transect suggest either continued input of contaminants to the environment or a minimal change in existing sediment conditions, due perhaps to limited distribution and dispersion of bottom sediments at transects 95 and 136 (UGLCCS, 1988). The same level of effect observed for transect 95 in 1994 was also apparent in toxicity tests completed in 1990 (Bedard and Petro, 1992a).

A comparison of 1994 and 1995 toxicity data for four individual stations, showed a marked similarity (Figure 5). Kendall's concordance test found strong agreement between several endpoints. Significant findings were found for mayfly mortality ($r = +.77$, $p = .0.05$) midge growth ($r = +1.0$, $p = 0.04$) and minnow mortality ($r = +.91$, $p = .0.04$), further implying a consistency in the data. Precise field sampling methodology and the selection of sediments of primarily either low or high contamination likely contributed to the biological endpoints following suit. Intralaboratory test variability was consistent in part due to the similarity in sensitivity among different batches of test organisms in standard copper sulphate reference toxicant tests. These findings lend credence to the use of midge, mayfly and minnow toxicity tests in providing reliable toxicity data regarding site-specific sediment quality. The use of such rigorous test procedures may be warranted depending on the test organism and/or study area (Borgmann and Norwood, 1993).

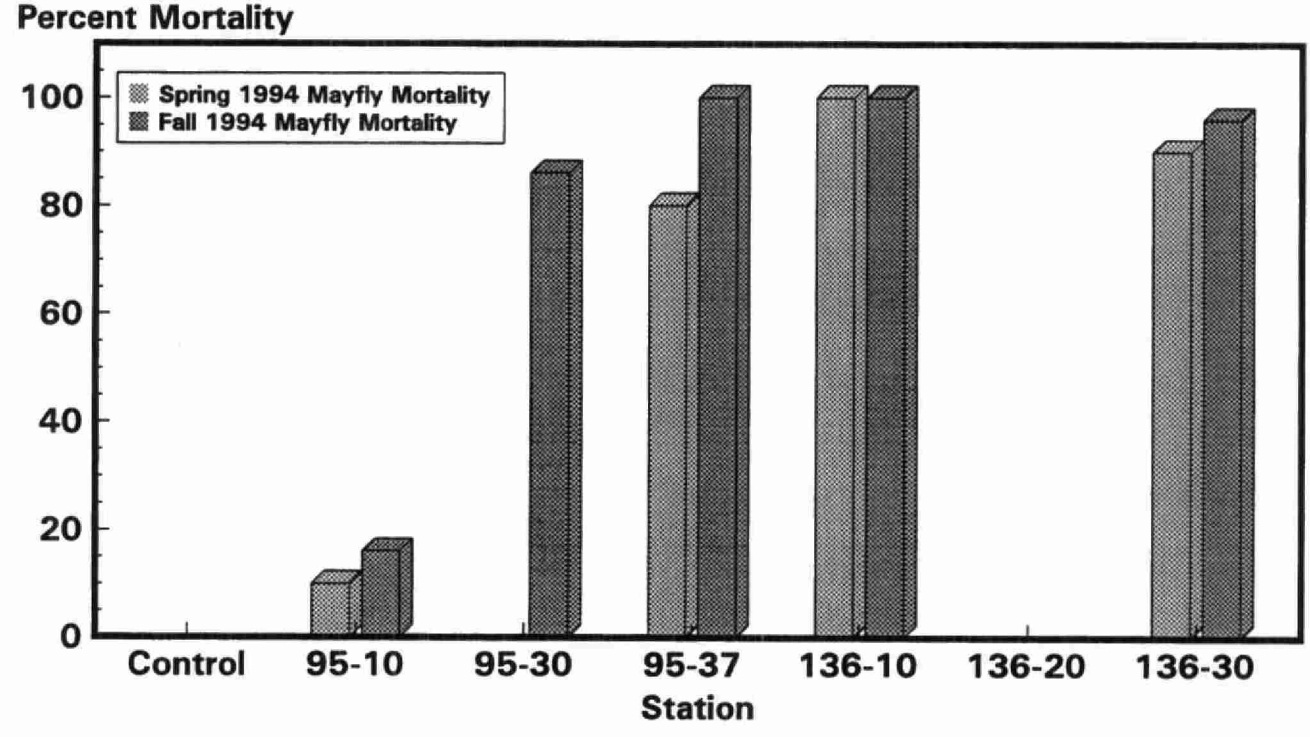
TABLE 10. Spearman rank correlation coefficients indicating significant positive (direct) correlations among toxicity data for spring 1994 St. Clair River sediments.

		Mayfly Survival	Mayfly Growth	Midge Survival	Midge Growth
Mayfly Growth	All Stations[a]	+ .837 ***			
	ESSO and Polysar Stns	+ .802 ***			
	Dow Stns	+ .865 **			
Midge Survival	All Stations	+ .605 **	+ .609 **		
	ESSO and Polysar Stns	+ .675 **	+ .647 **		
	Dow Stns	n.s.	n.s.		
Midge Growth	All Stations	+ .641 ***	+ .721 ***	+ .746 ***	
	ESSO and Polysar Stns	+ .745 ***	+ .784 ***	+ .825 ***	
	Dow Stns	+ .596 *	+ .709 *	+ .583 *	
Minnow Survival	All Stations	n.s.	n.s.	n.s.	n.s.
	ESSO and Polysar Stns	n.s.	n.s.	n.s.	n.s.
	Dow Stns	n.s.	n.s.	n.s.	n.s.

a ESSO and Polysar Stns include 134, 44, 73, 136, 45, 46, 94, 47 and 74 and Dow Stns include 134, 95, 48, 49 and 96.

* $p < 0.05$; ** $p < 0.001$; *** $p < 0.0001$; n.s. – Not Significant at p=0.05.

FIGURE 4. Organism Mortality for St. Clair River Sediment: Spring and Fall 1994



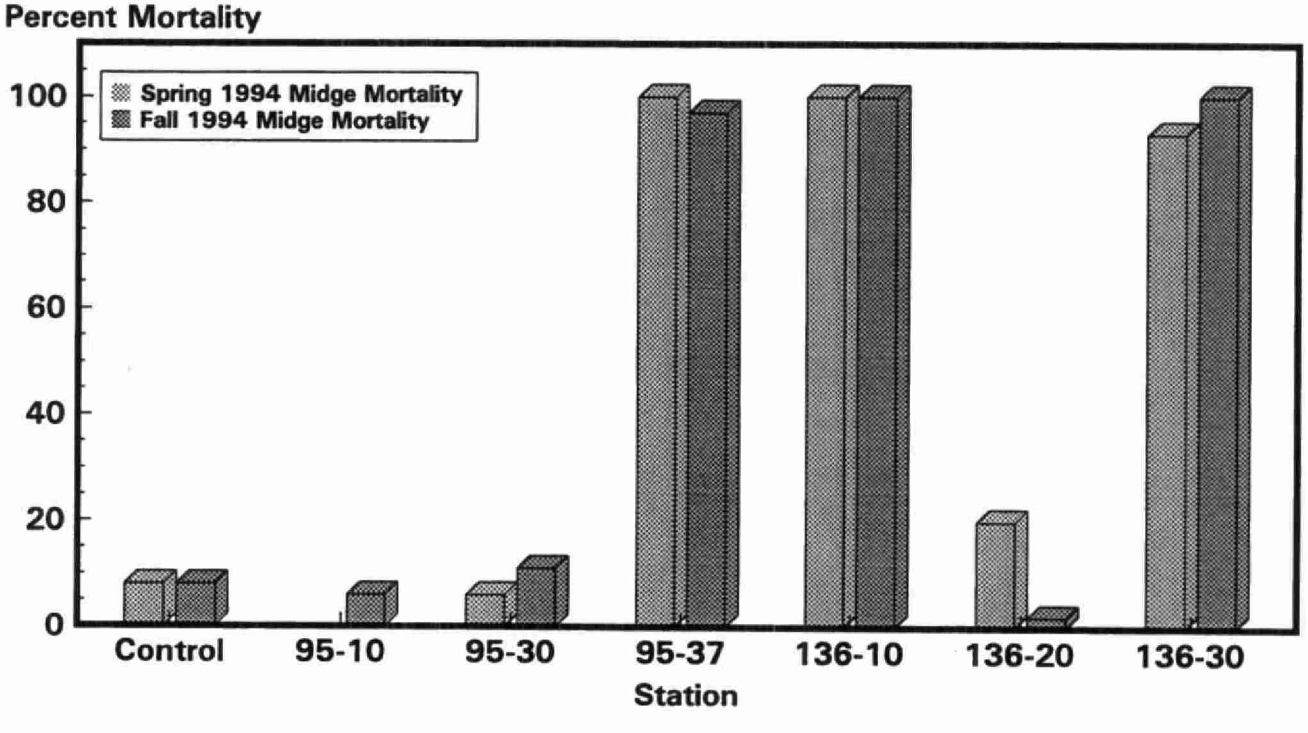
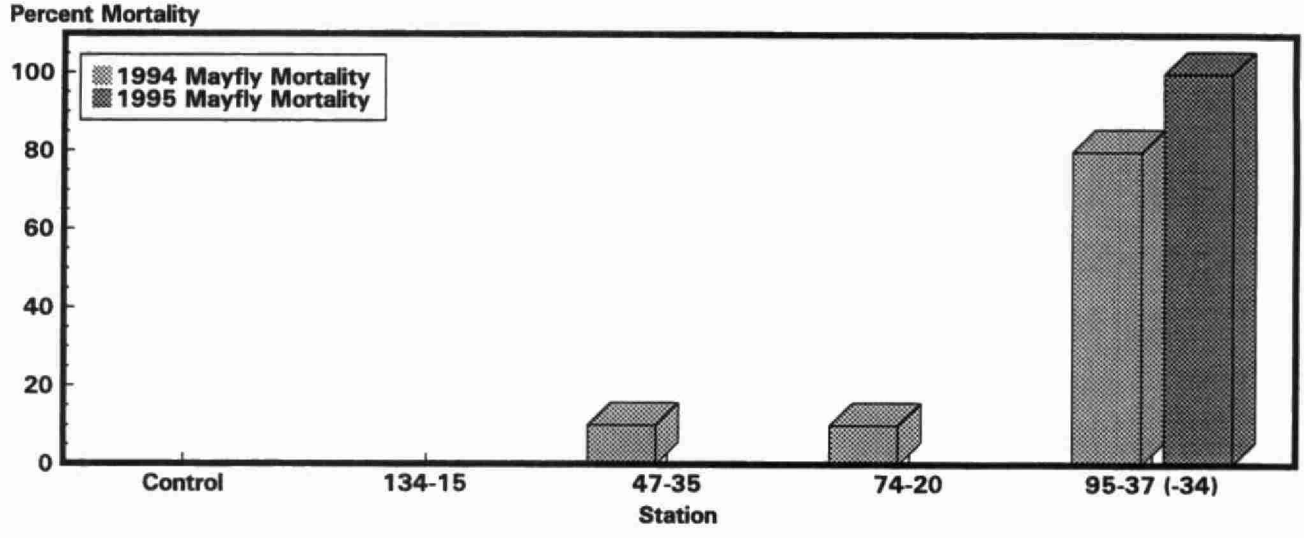
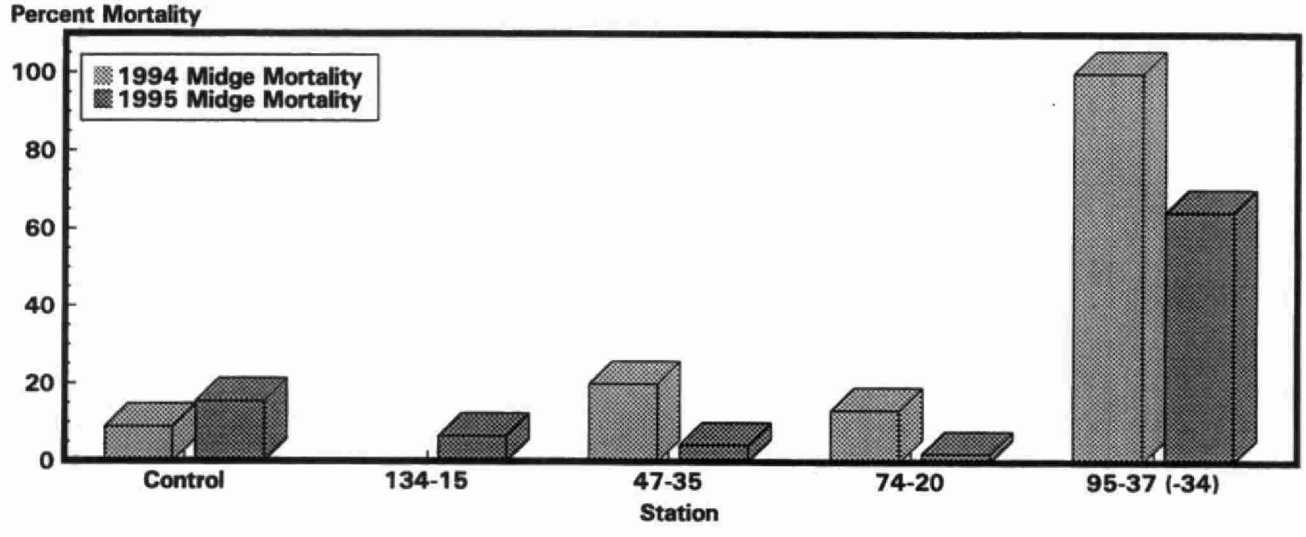
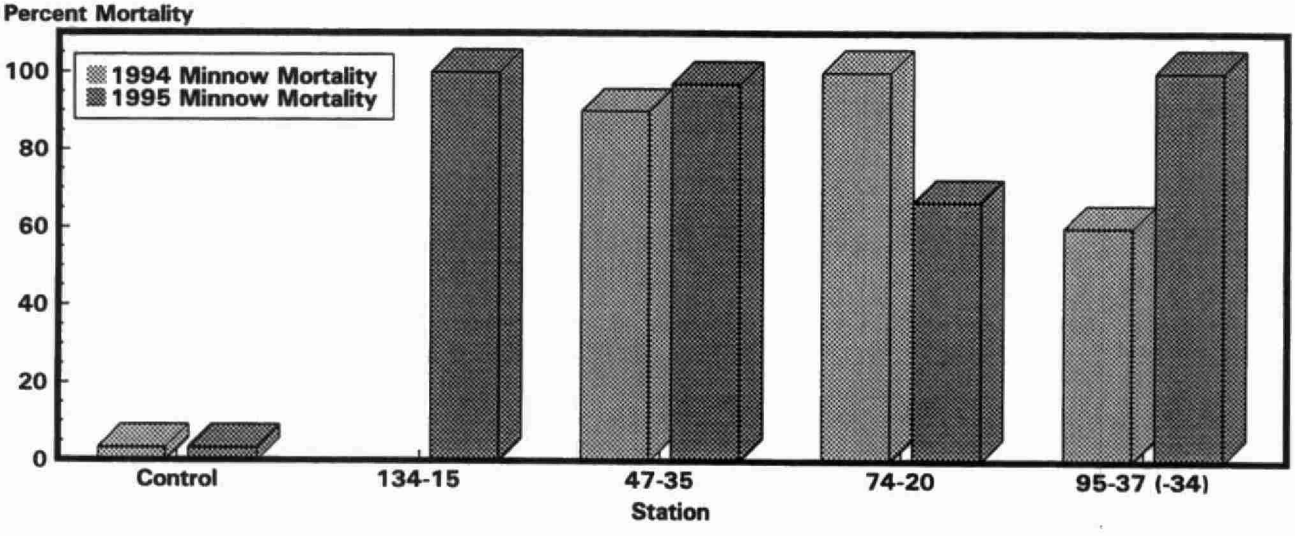


FIGURE 5. Organism Mortality for St. Clair River Sediment: 1994 and 1995







Relationships Between Biological Endpoints and Sediment Physical/Chemical Characteristics

Identification of potential causes for the observed laboratory effects showed mixed results for the spring 1994 study. The toxicity endpoints were compared to sediment physical, nutrient and chemical variables. Few significant negative (inverse) correlations were apparent when the entire 32 test sites were taken as a group (Table 11). Mayfly and midge survival and growth parameters matched most frequently, and to the greatest extent, with total PAH and solvent extractable sediment concentrations ($p < 0.05$ to 0.001). Both of these compound groups were ubiquitous in the study area as indicated by the level of background contamination in the upstream reference control sediment. The sum of the 16 measured PAH sediment concentrations failed to consistently reach toxic concentrations. Only Stn 47-35 approached the PSQG-SEL concentration of 250 μg/g (corrected for organic content) or the laboratory-predicted 50% lethality effects-level sediment concentration of 150 μg/g. The latter value is according to a number of previous sediment toxicity tests using PAH-contaminated sediments including those following a toxicity gradient (Bedard and Petro, 1993; Jaagumagi *et al.*, 1996). In fact, Stn 47-35 was not toxic to either benthic species. The remaining test sites were well below PAH effect-level concentrations and PAHs are not considered important toxic components of any of the test sediments.

The significant correlation between sediment solvent extractables concentrations and organism effects is probably indicative of a number of other compound(s) that co-occur with solvent extractables, rather than a direct consequence of any single chemical. Weaker correlations were noted between several CBs and fish mortality ($p < 0.05$).

Reexamination of the sediment chemistry revealed a distinct pattern in the distribution of organochlorine compounds. Higher sediment concentrations of chlorinated benzenes and toluenes dominated the Dow sites, as compared to the lower concentrations associated with the ESSO, Cole Drain and Polysar sites. This contrast in sediment chemical concentrations among sites could weaken the overall efficiency of the correlation analysis. Therefore, analysis was repeated after dividing the data set into two distinct groups.

Correlation analysis which focused only on the ESSO, Cole Drain and Polysar sites failed to improve the number of positive relationships or the associated level of significance (Table 11). As before, benthic survival was inversely correlated with sediment total PAH and solvent extractable concentrations. Organism toxicity among these sites was likely attributed to unidentified chemical compound(s) rather than PAHs, which were well below expected toxic concentrations. Several of the toxic sediments were characterized, both in the laboratory and during handling in the field, as being associated with a distinct chemical odour. The suspect chemical compound(s) associated with the sediment are likely to be fuel-like or petroleum-like and could have arisen from petrochemical facilities associated with the manufacture and refining of oil-based substances and aromatic derivatives.

There appears to be a relationship between organism toxicity and total petroleum hydrocarbon sediment concentrations. Compounds consisting of 15 to 50 carbon units fall within this group. Mortality of *Chironomus* and *Hexagenia* was lower at stations with total petroleum hydrocarbon concentrations ranging from non-detectable levels (100 μg/g) to 800 μg/g. Sediment toxicity was greater at Stns 73-10, 136-30, 46-25 and 74-30, where the total petroleum hydrocarbon concentrations ranged from 1500 to 4100 μg/g. This relationship did

TABLE 11. Spearman rank correlation analysis summary indicating significant negative (inverse) or positive (direct) correlation between biological endpoints and sediment physical and chemical parameters for spring 1994 St. Clair River samples.

Toxicity Endpoint	Mayfly Survival	Mayfly Growth	Midge Survival	Midge Growth	Minnow Survival
St. Clair River All Stations n = 39	– Total PAH *** – Solvent *** Extractables	– Total PAH ** – Solvent * Extractables	+ % Sand ** – Total PAH *** – Solvent *** Extractables	+ % Sand ** – TOC * – Total PAH *** – Solvent ** Extractables	– TEQ * – 1,2,3,4–tetraCB * – 1,2,3,5–tetraCB * – 1,2,4,5–tetraCB * – PentaCB * – HexaCB *
[a] ESSO and Polysar Stations only n = 27	– Total PAH ** – Solvent ** Extractables		+ % Sand ** – Total PAH ** – Solvent ** Extractables	+ % Sand * – Total PAH ** – Solvent * Extractables	– Total Nitrogen * – TEQ * – Solvent * Extractables
[b] Dow Stations only n = 15	– Total PAH * – Solvent * Extractables – TEQ ** – Hexachloroethane * – 1,2,4–triCB * – 1,2,3,4–tetraCB * – 1,2,3,5–tetraCB * – 1,2,4,5–tetraCB *	– Total PAH * – Solvent * Extractables – TEQ * – Hexachloroethane * – 1,2,3,5–tetraCB * – 1,2,4,5–tetraCB *	– Hexachloroethane * – Hexachloro– * butadiene – 1,2,4–triCB * – 1,3,5–triCB * – 1,2,3,5–tetraCB * – 1,2,4,5–tetraCB * – PentaCB * – HexaCB * – Octachlorstyrene *	– Total PAH ** – Solvent ** Extractables – TEQ * – Hexachloroethane * – 1,2,4,5–tetraCB *	+ Total Nitrogen * – Hexachloro– * butadiene – 1,2,4–triCB * – 1,2,3,5–tetraCB * – PentaCB * – HexaCB ** – Octachlorstyrene **

a Include Stns 134, 44, 73, 136, 45, 46, 94, 47 and 74.

b Include Stns 134, 95, 48, 49 and 96.

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

Correlation analysis did not include total petroleum hydrocarbon sediment concentrations due to an incomplete data set.

not apply to either of the ESSO sediments (Stns 44-30 and 44-45) and organism toxicity may have been a result of other unidentified organic compounds unique to this site.

Interestingly, those test sediments that contained higher amounts of sand-sized particles tended to actually improve midge larval growth and subsequently enhanced larval survival, thereby partially offsetting any adverse chemical impact that may have been present. The influence of substrate type on chironomid performance in toxicity tests is not uncommon but usually is not considered a major factor (Ankley *et al.*, 1994). Midge larvae tend to prefer coarser substrates which provide particles suitable for the construction of cases for their subsistence. As for the fathead minnow toxicity tests, the variables that correlated with minnow mortality differed from those derived for the entire study area, although the degree of significance remained relatively low ($p < 0.05$). Minnow survival was negatively correlated with sediment TKN concentrations, possibly implying a negative effect due to ammonia production.

The isolation of the Dow locations in the correlation analysis substantially increased the resolution in measuring significant responses between the biological and chemical parameters. Several new correlations emerged and included significant relationships between HCE, tCBs, teCBs, QCB, HCB and OCS sediment concentrations with lethal and sublethal effects for each organism. Generally, higher sediment concentrations for these chemicals were associated with the Dow site as compared to the upstream test locations. Among these organic compounds, only HCB is currently classified as a toxic substance under CEPA (EC, 1993), listed as a banned substance under OMOE (OMOE, 1992b) and is of restricted use under IJC (IJC, 1989). Substantial effects-level and bioaccumulation data exist for HCB in the literature. Limited toxicological information exists for the other chemicals and the exact extent of the environmental harm is currently unknown, particularly from contaminated sediments. Compounds such as CB, HCBD, HCE and QCB do appear on the OMOEE secondary list of chemicals destined for phase-out (OMOE, 1992b).

Ontario sediment quality guidelines have been developed for only one of the chlorinated benzenes. The PSQG-SEL concentration in sediment for HCB is 24 μg/g, dry weight (Persaud *et al.*, 1992). After correction for sediment organic content, the sediment concentrations along transects 95, 48, 49 and 96, exceed the PSQG-SEL concentration at each station. In comparison, among the upstream test sites, only the transect below Polysar (transect 74) consistently exceeded SEL concentrations for HCB but at reduced concentrations. For the Dow sediments, after plotting toxic and non-toxic responses relative to sediment HCB concentrations, the SEL concentration (uncorrected) did not accurately predict the occurrence of a toxic response in mayflies, midges or fathead minnows (data not shown). Raw sediment data was graphed since no significant correlation existed between HCB sediment concentration and sediment TOC ($r = +0.43; p < 0.15$) nor with percent sand ($r = +0.01; p < 0.98$). A similar relationship was observed for CBs in Detroit River sediment (Kaiser *et al.*, 1985; Platford *et al.*, 1985). Obviously, other site-specific factors such as the added stress of multiple contaminants will contribute to the overall biological effect. These effects are likely to be additive since several CBs have been shown to share a similar mode of toxic action (McCarty *et al.*, 1992a).

The Dow data set was also subjected to linear regression analysis to further quantify any possible dose-response relationships for single compounds. Midge mortality significantly

regressed with HCB, HCBD, QCB and OCS bulk sediment concentrations. The best relationship occurred for HCBD with 94% of the variation in midge mortality being explained by HCBD bulk sediment concentrations (Figure 6). The 10-day midge LC50 was 63 μg/g (54 - 75 μg/g 95% C.I.), after the removal of one outlier from the equation. At the same exposure concentration, a minimum of 20 % mortality to mayflies was reported at four of the stations in 21-day toxicity tests. Approximately the same effects-level sediment concentration that was reported for HCBD also applied to HCB in the midge toxicity test. The 10-d LC50 for HCB was 91 μg/g (73 - 117 μg/g 95% C.I.) with 89% of the variation explained (Figure 7). Significant linear regression was also noted for OCS ($p=0.0005$; $R^2=85$) and QCB ($p=0.0004$; $R^2=89$) with *C. tentans* survival.

Weaker regressions were apparent for the mayfly toxicity data with only 54% and 52% of the variation in mortality described for sediment HCBD and HCB, respectively. This is likely a consequence of the quality of the toxicity data. Mayflies appear to be a more sensitive test organism and followed an all or none type of response with fewer partial mortalities being reported, and created a certain degree of instability in the regression procedure.

In an attempt to strengthen the relationship between organism mortality and sediment concentration, compounds sharing similar physico-chemical properties were considered as a group rather than as individual compounds. There are several explanations that justify and support the importance of examining chemical mixtures in bulk sediments (Hoke *et al.*, 1993; Carr *et al.*, 1996). First, chlorinated benzene compounds are classified as non-polar, halogenated compounds that produce narcosis in a variety of aquatic species (McCarty *et al.*, 1992b). The joint toxicities of these types of nonreactive compounds are additive because they share the same toxic activity (McCarty *et al.*, 1992a). Several of these compounds were shown to co-vary in the spring 1994 sediment samples collected downstream of Dow 1st Street sewer (data not shown).

Second, the magnitude of chemical exposure is generally greater for those chemicals found at the higher concentrations in the sediment (Schrap and Opperhuizen, 1990). Higher Kow organic chemicals normally have a stronger affinity to sorb to particulate matter as compared to lower Kow compounds (Oliver, 1987; Oliver and Bourbonniere, 1985). The relative chemical concentration in the Dow sediments generally coincided with the chemical partitioning coefficient. For example, sediment concentrations were highest for HCB, HCBD, OCS and QCB and log Kow values exceeded 4.8. Loading estimates from Dow discharge points followed a similar pattern and will influence overall sediment concentrations in the area (OMOE, 1992a).

Third, chemical properties assist in describing the likelihood of its' availability to biota. Chemicals that are more persistent will subsequently result in increased exposure and uptake. Oliver (1987) measured the presence of lipophilic compounds in several phases in sediment laboratory experiments, including aqueous (overlying water, interstitial water) and particulate phases (suspended sediment, bedded sediment). Conversely, the more water soluble and volatile compounds such as HCE, toluene and the less chlorinated CBs are liable to be found at reduced concentrations, particularly in the solid phases (EC and OMOE, 1986; Oliver and Kaiser, 1986; Chan *et al.*, 1986). A direct comparison of sediment chemical concentrations between the 1995 field and laboratory sediment samples succinctly demonstrated the potential loss of less hydrophobic contaminants. It is assumed that exposure concentrations

FIGURE 6. Regression Analysis of Midge 10-d Percent Mortality on Bulk Sediment Hexachlorobutadiene Concentration for Transects 95, 47, 48 and 96

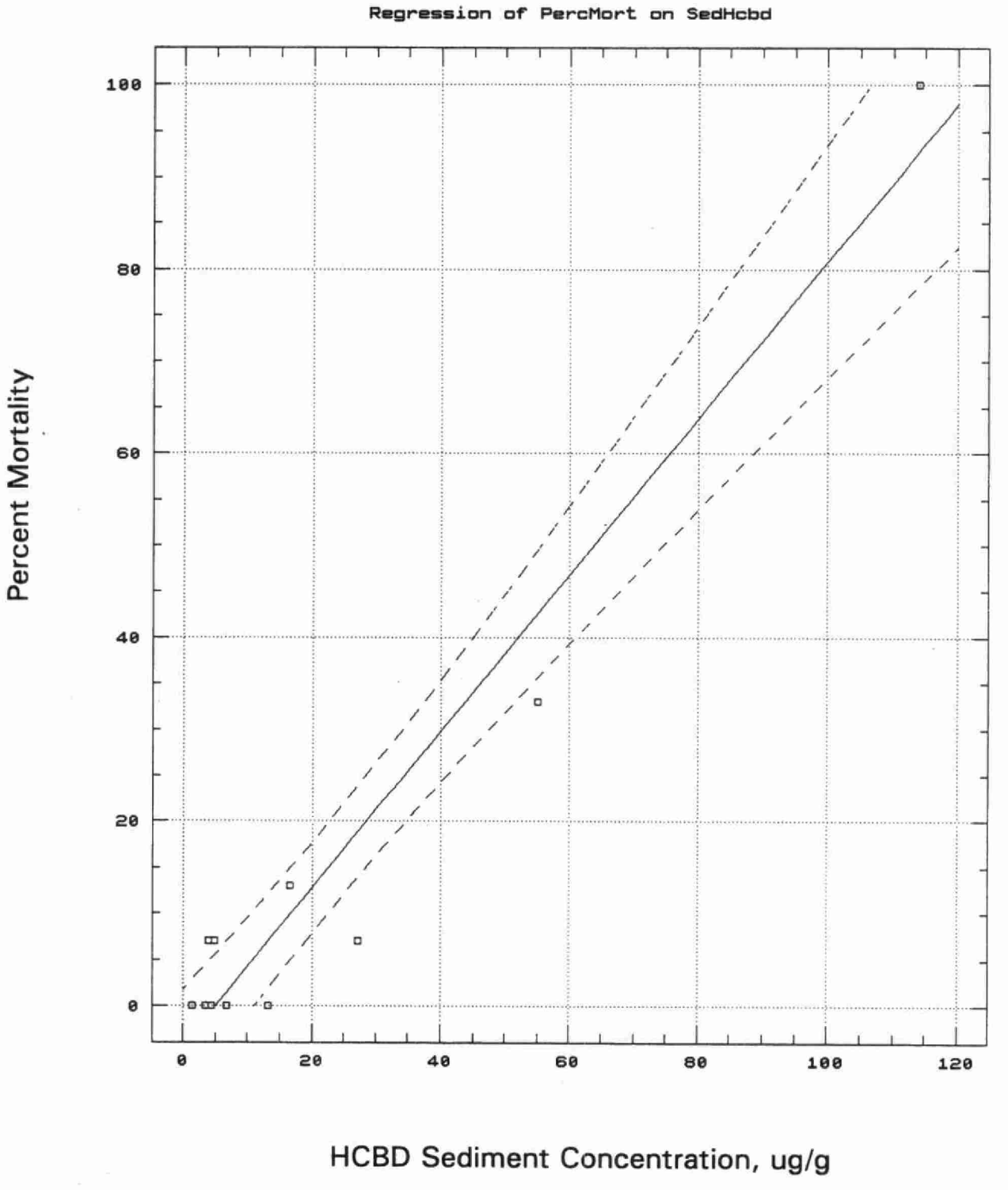
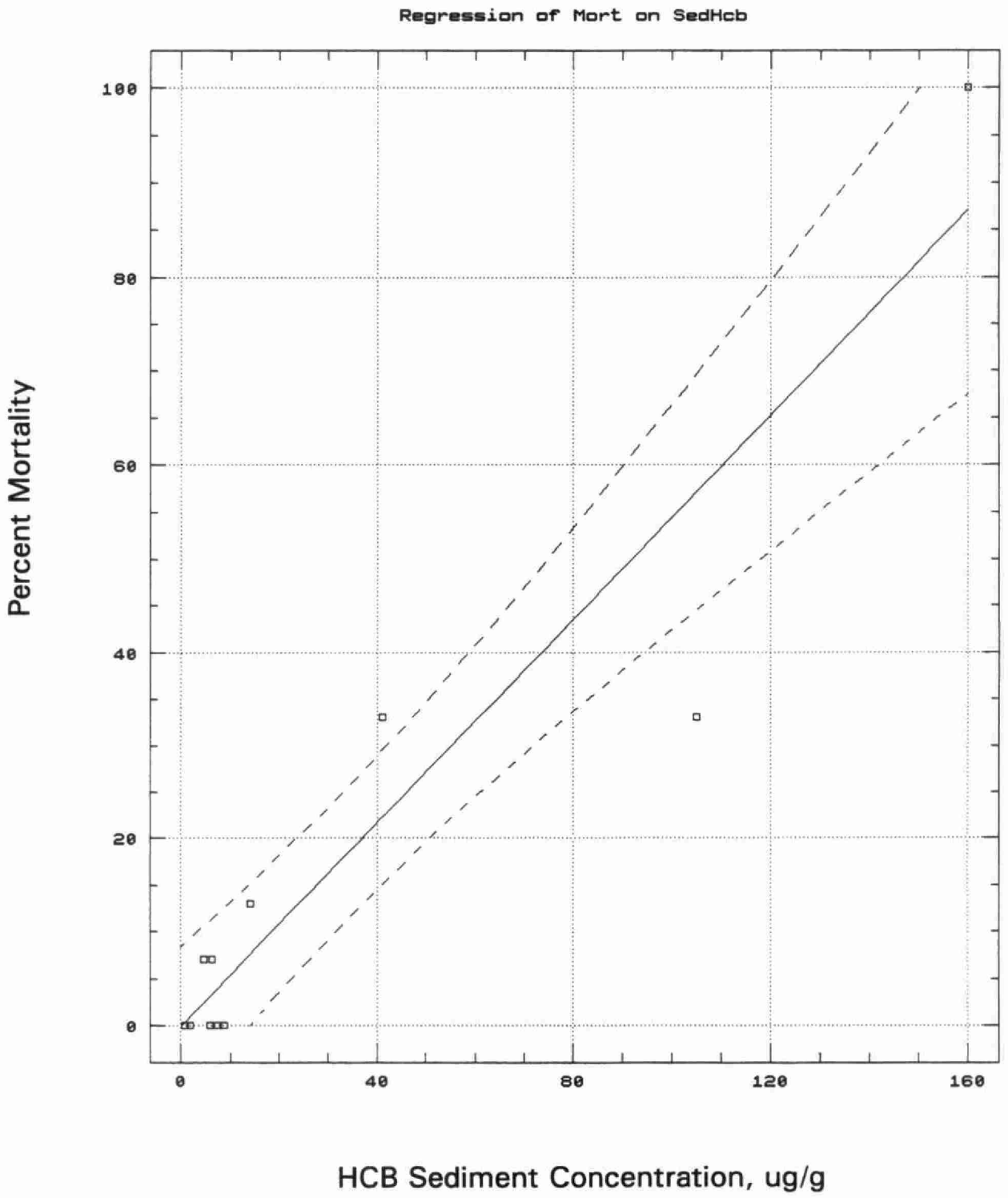


FIGURE 7. Regression Analysis of Midge 10-d Percent Mortality on Bulk Sediment Hexachlorobenzene Concentration for Transects 95, 47, 48 and 96



were significantly reduced in the sediment toxicity tests, depending on the chemical properties of these compounds.

Fourth, it has been shown repeatedly that higher Kow or lipophilic organic chemicals such as HCB, OCS and QCB attain higher tissue concentrations in aquatic biota exposed in the field (Kauss and Hamdy, 1985; Pugsley *et al.*, 1985; Suns *et al.*, 1991). Similarly, under laboratory conditions, Drouillard *et al.*, (1996) observed a direct correlation between the rate of uptake of sediment-sorbed contaminants with chemical Kow for mayflies, and Oliver (1987) for oligochaetes. Higher Kow compounds can bioaccumulate in biota because of lower depuration rates (Konemann and Van Leeuwen, 1980; Oliver and Niimi, 1985; Lydy *et al.*, 1992). In this study, chemical concentrations appear to have reached sufficient concentrations over a relatively short period of time in fathead minnows and tended to reach higher HCB and OCS tissue concentrations than those measured in the field for bottom-dwelling fish species, including sculpins (OMOE, 1991) and spottail shiners (Suns *et al.*, 1991). This increases the chances that lethal concentrations for the same group of chemicals also occur in the other test animals (Ankley *et al.*, 1992; Lester and McIntosh, 1994).

To better address the combined effects of multiple contaminants on the test organism(s), additional regression analysis was completed between organism lethality and a sum of the sediment concentrations for HCBD, OCS, HCB and QCB for transects 95, 48, 49 and 96. After the removal of two outliers, Stns 95-30 and 48-37, as much as 98% of variation of midge mortality was successfully explained. The resulting 10-d midge LC50 for the combined group of four chemicals was 147 μg/g, dry weight (Figure 8). The 95% confidence intervals were quite narrow, at 134 to 161 μg/g. Similarly, for mayfly lethality, after the omission of Stns 95-30 and 49-40, the 21-day mayfly LC50 was 162 μg/g for the sum of HCBD, OCS, HCB and QCB (Figure 9). The corresponding upper and lower 95% C.I. were 111 μg/g and 249 μg/g and the $R^2 = 80$, which is a solid improvement relative to any of the single-compound relationships.

Inorganic contamination of the Dow sediment samples also needs to be considered as a possible source of toxicity. Mercury is persistent, toxic, carcinogenic and is an environmental concern (NRCC, 1979). Bulk Hg sediment concentrations surpassed the PSQG-SEL of 2 μg/g at all Dow stations with the exception of Stn 95-37. Sediment concentrations were as much as 80 times higher than the SEL criteria but no significant relationship was found with any of the lethal and sublethal toxicity test responses. Similar sediment Hg concentrations were reported in 1990 in the same stretch of the St. Clair River and is known to have some of the highest Hg sediment concentrations for large water-bodies and rivers in Ontario (Jaagumagi, 1988). In spring 1994 the average sediment Hg concentrations for transect 95 was 4 μg/g, transect 48 was 30 μg/g, transect 49 was 97 μg/g and transect 96 was 20 μg/g. Several toxicity studies using mayfly nymphs (*H. limbata*), midge larvae (*C. tentans*) and fathead minnows (*P. promelas*) exposed to Hg contaminated sediment at substantially lower concentrations, failed to demonstrate any significant lethal organism response (Bedard and Petro 1992b; 1992c; 1992d). The sediments were collected from the St. Lawrence River and had a maximum Hg sediment concentration of 7 μg/g; Peninsula Harbour with a concentration of 5 and 9 μg/g; and a lake in northern Ontario impacted by mining activities with reported maximum concentrations of 12 and 18 μg/g. Among these studies, the noteworthy harmful response was reported for midge growth which was significantly reduced at an exposure concentration of 7.5 and 18.0 μg/g, but not at

FIGURE 8. Regression Analysis of Midge 10-d Percent Mortality on Sum of Bulk Sediment HCBD, HCB, QCB and OCS Concentrations for Transects 95, 47, 48 and 96

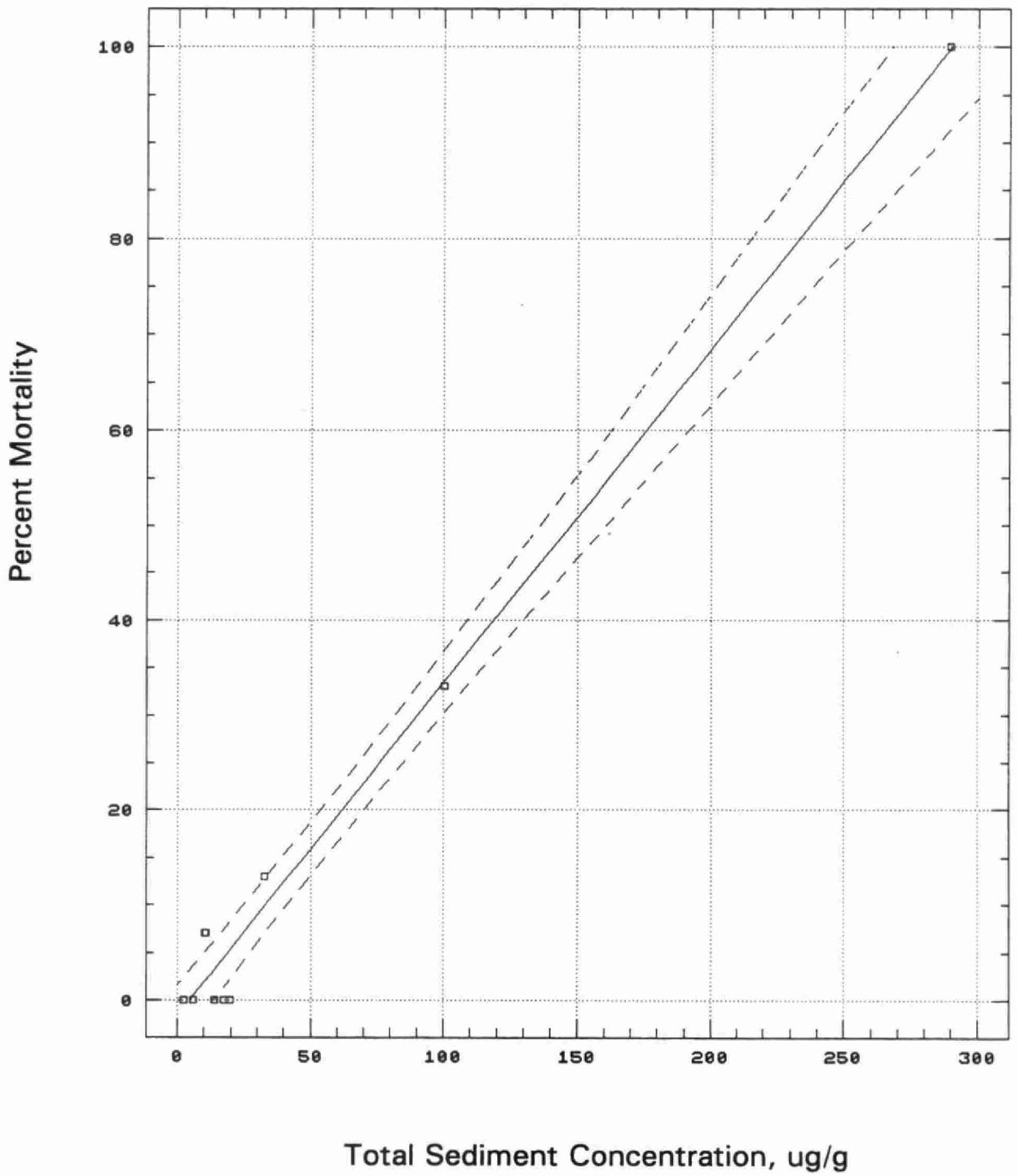
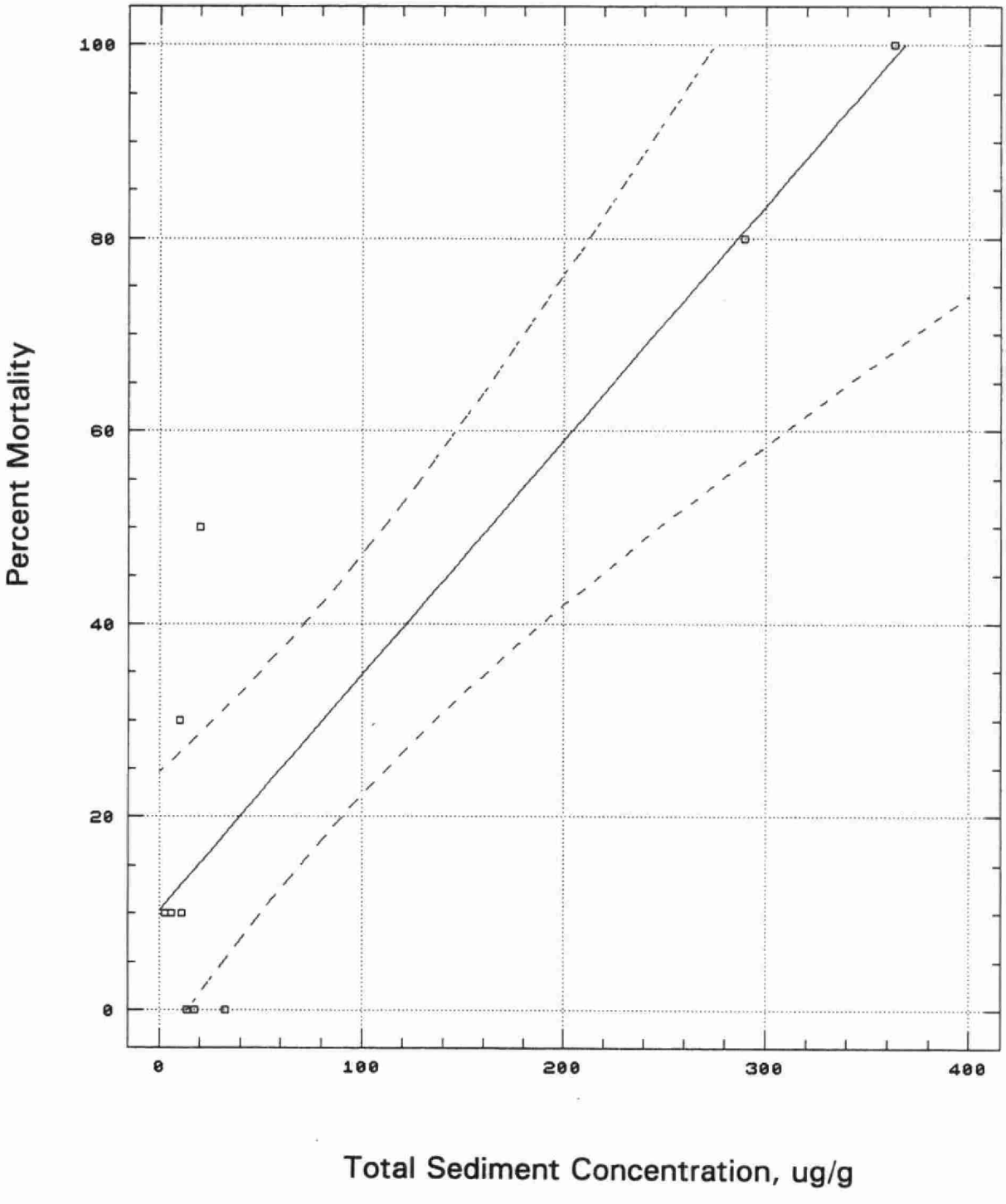


FIGURE 9. Regression Analysis of Mayfly 21-d Percent Mortality on Sum of Bulk Sediment HCBD, HCB, QCB and OCS Concentrations for Transects 95, 47, 48 and 96



concentrations of 5.3, 9.8 or 12.0 μg/g. Odin *et al.*, (1994), reported that after a sediment exposure to 10 μg/g Hg (dry wt) for 15 days, the mayfly *Hexagenia rigida* did not exhibit significantly reduced survival or growth. Given these findings it is likely that the markedly elevated Hg sediment concentrations (> 20 μg/g) found at 58% of the Dow stations are exerting metal-related stress to the organisms, particularly to the midge, *C. tentans*.

Comparison of Lethality with Residue-based Concentrations

The above four-compound regression analysis derived an LC50 concentration based on bulk sediment, which often does not necessarily accurately represent the available chemical concentration for sediment-sorbed organic contaminants (Landrum *et al.*, 1994). A better and more accurate predictor of organism toxicity can be determined by the critical body residue or CBR (Landrum *et al.*, 1992). The CBR is an internal organism tissue chemical concentration that once reached, death ensues and is often referred to as the lethal dosage, if it is measured at the time of death. Several authors have cited values (based on wet weight) of 4.0 mM/kg (McCarty *et al.*, 1992a), 2.8 mM/kg (Van Leeuwen *et al.,* 1992) and 2.5 mM/kg (Van Hoogen and Opperhuizen, 1988), depending upon the exact endpoint used, be it the LC50 (CBR) or time of death (lethal dose). Since the CBR is dependent on the site of toxic response in an organism, it is treated as a constant and is independent of the time of exposure and does not require that the external chemical concentration be at equilibrium, as was the case for tests using spiked-water (Sijm *et al.*, 1993) or spiked-sediment (Landrum *et al.*, 1994). Therefore, it would be interesting to compare the observed LC50 bulk sediment concentration measured for the Dow sediment samples with a predicted LC50 sediment concentration through the use of existing CBR data. This can be achieved by applying the concept of equilibrium partitioning theory for chemicals that are classified as being non-reactive, narcotic chemicals e.g. chlorinated benzenes, which appear to be of the greatest toxicological significance in the Dow sediments.

The large body of work that exists on CBRs for organic narcotic substances has pertained solely to fish and water exposures, where there is a well established relationship between a chemicals' water solubility and its' uptake by fish from a single route of exposure, as defined by quantitative-structure activity relationships or QSARs (Veith *et al.*, 1983; McCarty, 1986). On the other hand, less is known about CBR as it relates to sediment/benthos interactions on naturally contaminated toxic sediments. Although tissue body burdens were not measured in either the midge or mayfly assays, the use of the CBR in conjunction with the calculated LC50s could aid in determining sediment concentrations expected to cause toxicity. According to the work by McCarty (1986), the CBR is a result of a chemical partitioning between water and the lipid component of the fish. The same concept can be applied to any invertebrate and sediment sample, assuming the chemical is obtained primarily from the sediment. In this case, instead of the chemical partitioning between water and fish lipid, one can suppose the chemical will partition between the organic content fraction of the sediment and the lipid fraction of the invertebrate. Reuber *et al.*, (1987), has shown TOC and lipid to have a similar affinity for organic chemicals over a wide Kow range. Therefore, the internal tissue concentration or CBR and the external sediment LC50 concentration (referred to as LSC) should be approximately equivalent.

The CBR values previously cited (Van Hoogen and Opperhuizen, 1988; McCarty *et al.*, 1992a; Van Leeuwen *et al.*, 1992) are based on an average fish lipid content of about 5%;

however, the lipid content of mayfly nymphs and midge larvae is somewhat lower and an adjustment is required. Literature values will serve as estimates; Harkey *et al.*, (1994a) cite a value of 3.7% for cultured *Chironomus* larvae and Drouillard *et al.*, (1996) 2.1% for laboratory-reared mayflies. Thus, a CBR based on 2% organism lipid would yield a value ranging from 1.0 to 1.6 mM/kg (wet weight). Along the same lines, the LSC should be established on the average TOC of the Dow sediments which was 1.1 %, thereby yielding a similar number, and the CBR and LSC can be used interchangeably. In addition, because each of the organic chemicals of concern are classified as narcotic substances and share a similar mode of non-specific toxic action, the CBR (or LSC) would be identical whether it is used on single compounds or as a mixture (McCarty *et al.*, 1992b). The average molecular weight for HCBD, HCB, OCS and QCB is 257 ± 20. The calculated CBR (or LSC) for this group of chemicals which is expected to explain the majority of the toxicity, is 326 to 522 μg/g (converted to dry weight).

There seems to be fairly good agreement between the expected (326 to 522 μg/g) and the observed sediment LC50 concentrations of 147 to 162 μg/g, given the associated levels of uncertainty. The sediment lethal concentration derived in this study (1.0 to 1.6 mM/kg) is not unlike those obtained for PAH-spiked sediments by Landrum *et al.*, (1991; 1994) which found a sediment LC50 concentration of 0.7 - 1.1 mM/kg. The author subjected the amphipod, *Diporea*, to a series of spiked sediments over a 30 day period and directly measured chemical tissue concentrations relative to amphipod survival rates. The slightly smaller sediment LC50 may have been due to the large differences in lipid content between the amphipod (25% lipid) as compared to our test species (~2% lipid). Nevertheless, this approach appears to substantiate the relationship between toxicity and exposure through the use of tissue concentrations whether it is used under controlled, aqueous flow-through conditions or for more complex static, sediment tests.

One area of potential error is in the derivation of the sediment LC50 concentration, which is based on field sediment chemistry and may have overestimated that chemical concentration tested in the laboratory toxicity tests. In addition, the current study was not purposely designed to measure a dose-response relationship or necessarily to test sediments from a gradient of sediment chemical concentrations. The relatively small sample size of 12 stations would also limit the derivation of a sediment LC50 concentration, although sediment concentrations did encompass sediments of low, intermediate and high chemical concentrations. Other experimental designs involving a dilution or spiked-sediment series may better address such relationships (ASTM, 1995). Also, the CBR (or LSC) is obviously sensitive to changes in either organism percent lipid or sediment TOC. For example, using a normalizing factor of a lower value of 1% would result in a LSC of 163 to 261 μg/g, which is in closer agreement to observed sediment LC50 concentrations for either single or multiple chlorinated organic compounds.

A violation of the assumption that sediment acts as the sole route of chemical exposure would alter the ratio between internal and external chemical concentrations. The simple relationship that the chemical concentration in the animal is equivalent to that associated with the sediment gives a reasonable first approximation of the LSC, in other words being at unity. If one takes into account multiple routes of exposure then the CBR will exceed the LSC. According to several studies, the internal tissue chemical concentration typically surpasses the sediment chemical concentration by a factor of 1.7, or LSC = 1.7 x CBR, for compounds such

as HCB (Lake *et al.*, 1990; Van Leeuwen *et al.*, 1992; Boese *et al.*, 1995). This will provide a revised LSC of 191 to 307 μg/g (dry wt).

Finally, the LC50 sediment concentrations measured for individual chemicals, such as HCB 91 μg/g in the midge assay, is underestimated by that projected by the CBR. Therefore it appears evident that multiple chemicals, rather than a single compound, are responsible for the measured toxicity.

Intrinsic Factors Affecting Chironomus and Hexagenia Lethality and Growth

Several factors may account for the species-specific differences in sensitivity between the two invertebrate species. Overall, the St. Clair River sediments were more toxic to *Hexagenia,* resulting in a higher frequency of moderate and high levels of toxicity, as compared to *Chironomus*. Exposure duration, feeding behaviour and routes of chemical exposure between the midge and mayfly likely played a role in explaining these differences (Thomann *et al.*, 1992). Midge larvae dwell at the sediment-water interface and obtain a large portion of their diet through the grazing of food provided during the test and lesser amounts from bacteria found in the surrounding water and naturally-occurring organic matter associated with the sediment (Suedel and Rodgers, 1994; Ankley *et al.*, 1994). Mayflies are benthic and continuously ingest sediment particles, algae and detrital matter and probably have a higher exposure of sediment-sorbed contaminants (Hanes and Ciborowski, 1992; Boese *et al.*, 1995). Harkey *et al.*, (1994b) found the amphipod, *Diporea*, a selective-feeder, consistently accumulated several hydrophobic organic contaminants from lab-spiked sediment to a greater extent than *Chironomus riparius*, a filter feeder, in side by side bioassays. Mayfly nymphs also have an elaborate gill structure to enhance chemical uptake via interstitial water during respiration, along with the capacity to acquire contaminants through the gut, thereby increasing exposure potential (Landrum and Poore, 1988; Gobas *et al.*, 1993). There is also evidence to suggest that the integument of *Hexagenia limbata* acts as an additional route of uptake from water, e.g. interstitial water (Stehly *et al.*, 1990). Routes of exposure to the midge are limited to the overlying water and to a lesser extent to the interstitial water (Adams *et al.*, 1985). Toxicokinetic studies using mayflies and spiked or field-contaminated sediments support the relative importance of sediment as a source of chemical bioaccumulation for hexchlorobiphenyl and PAH compounds (Landrum and Poore, 1988), hexachlorobenzene (Bedard, 1990) and HCB, OCS and PCBs (Drouillard *et al.*, 1996). These studies have shown *Hexagenia limbata* obtains over 90% of the chemical body burden from sediment. Gross physical sediment attributes, e.g. % sand, TOC, which may inhibit proper burrow formation by mayflies causing abnormal stress, did not appear to be a direct factor (Table 11). Other studies have found delayed mayfly mortality under conditions of unsuitable substrate type (Bedard and Petro, 1992a). In this study, the majority of the toxic sediments resulted in an immediate avoidance reaction, which is not characteristic of non-chemical stress.

Maximum chemical uptake and bioaccumulation will vary with chemical properties, particularly Kow, along with exposure duration. In a recent study on Detroit River sediments, Droullard *et al.*, (1996), estimated 95% of steady-state conditions were achieved for *Hexagenia* exposed to several organic compounds within 32 to 33 days. The standard 10-day test length used in the midge assay may have underestimated equilibrium conditions relative to the longer 21-day test used for the mayfly assay. The former is required due to the relatively short life span of *Chironomus tentans*. A standard exposure period of 28 days is

recommended for performing chemical bioaccumulation studies on bed sediments which typically provides at least 75% of steady-state (ASTM, 1995; Boese *et al.*, 1995).

Factors Affecting Pimephales Lethality

Fathead minnow mortality responses differed significantly from those of either of the benthic organisms, except at four stations where sediments were deemed toxic for all three test organisms, suggesting equal sensitivity to a common factor. In an interesting study, Ankley *et al.*, (1991) observed that a number of lethal sediments collected from the Detroit River were toxic to <24 hour-old *Pimephales promelas* larvae regardless of the media tested e.g. bulk sediment, elutriate or pore-water fractions. This indicates that for some highly contaminated sediments, pelagic species exposures will more closely represent those encountered by benthic species, thereby perhaps explaining the similarity among test species at Stns 136-10, 136-30, 44-30 and 95-37.

Other explanations are needed that will aid in interpreting the outstanding disparities in toxicity between fish and benthos. These would pertain to differences in the route of chemical exposure, feeding strategy and chemical sensitivity. The ability to avoid the sediment and mode of feeding will subsequently alter the relative exposure concentration to fish relative to the benthos. Exposure to extracts from sediments, especially interstitial water, appears to be more toxic than those assessed using the bulk sediment, probably because of lower chemical concentrations associated with the overlying water, as was cited by Ankley *et al.*,(1991) for a number of Detroit River sediments tested with fathead minnows. In other words, for some test sediments there could be differences in chemical exposure between those organisms with a closer association with the overlying water relative to those in direct contact with interstitial water, thereby suggesting benthic invertebrates are subjected to higher chemical concentrations. It is expected that the work by Ankley *et al.*, (1991) should be a good representation of the types of contaminants encountered in this study.

At all of the 1994 St. Clair River sites causing 100% fish mortality, a subsample of the unfiltered overlying water was submitted for chemical analysis to determine if HCB was common to all the toxic samples. The data was not directly comparable, partly due to the differences in the time interval at which the sample was removed. Time points ranged from 13 to 21 days, with most of samples taken by Day 15. Chemical analysis revealed HCB water concentrations ranged from non-detected to a maximum concentration of 0.30 μg/L. This value is well below the solubility concentration of 5 μg/L, which is non-lethal in 28-days to fathead minnows, worms and amphipods (Nebeker *et al.*, 1989) and in early-life cycle stage assays for fathead minnows (Carlson and Kosian, 1987).

Other operable factors known to be lethal to fish need to be considered. Fish are more sensitive to un-ionized ammonia concentrations as compared to benthic organisms (Hellawell, 1986). The 1995 study supports this idea quite clearly, with minnow survival severely affected at all of the test sites, even the reference site. On the other hand, no adverse lethal effect was evident in either of the benthic toxicity tests. The main dissimilarity in chemical parameters among samples occurred for un-ionized ammonia concentrations measured in the overlying water. Concentrations at or above 0.79 mg/L NH_3 reported in the minnow assay, were found to be significantly correlated with fish mortality, $r=0.94$; $p<0.03$. The acute effect concentration range reported by Thurston *et al.*, (1986) is 1.27 - 2.73 mg/L NH_3, cited

as a 96-hour LC50, for fathead minnows of similar age and test conditions. Although the time-averaged un-ionized ammonia concentration was lower than the acute effects-level concentration, continuous exposure at these sublethal concentrations could elicit such a toxic response. Peak concentrations were measured by Day-10, at an average concentration of 1.50 ± 0.45 mg/L NH_3, and approach concentrations that are above the tolerance range for *Pimephales promelas* (Thurston *et al.*, 1986). This time frame also coincided with the initial loss of minnows in both the 1994 and 1995 toxicity tests, suggesting a gradual increase in ammonia preceded minnow death. Benthic species such as the midge, *C. tentans* and the worm, *Lumbriculus sp.*, have a considerably higher tolerance to un-ionized ammonia concentrations and are generally more resistant to changes in ammonia (Schubauer-Berigan *et al.*, 1995).

In the spring 1994 study, average un-ionized ammonia in the minnow toxicity test remained between 0.02 and 0.19 mg/L and represents a value calculated among sites pooled across a transect. Fish mortality was site-specific rather than transect-specific and exact ammonia levels at each site were not provided. Although conclusive evidence is not available for the individual spring 1994 samples, average un-ionized ammonia concentrations were higher for sediments collected along transect 94, and may partially account for the high toxicity to minnows at Stns 94-10 and 94-25 and the significant correlation between total TKN sediment concentrations and fish mortality (Table 11). The presence of ammonia in sediments may arise from the nitrification of bottom organic material through microbial degradation or from industrial effluents containing ammonium compounds related to industrial processes (Russo, 1985; Ankley *et al.*, 1990).

Importance of Organic Chemical Bioavailability and Bioaccumulation

Chemical bioaccumulation of organic chemicals by fathead minnows in the spring 1994 survey was not definitive due to the need to combine surviving animals across a transect. Nevertheless, the data did reveal some general trends in chemical uptake. Even though several chlorinated organics were detected in the sediment at measurable levels, only pp-DDE, PCBs, HCB, QCB, OCS and HCBD were accumulated above trace amounts in the test minnows. Numerous field studies have documented the tendency for CBs and OCS to accumulate at several trophic levels in the aquatic food chain of the St. Clair River and Lake St. Clair. Aquatic biota include native mussels (*Lampsilis* sp.) (Pugsley *et al.*, 1985), introduced mussels (*Elliptio* sp.) (Kauss and Hamdy, 1985), indigenous benthic invertebrates (Gobas *et al*, 1989; OMOE, 1991), emergent adult insects (Ciborowski and Corkum, 1988), forage fish (OMOE, 1991; Suns *et al.*, 1991) and sports fish (EC and OMOE, 1986).

This selective uptake of certain chemicals appears to be related to the relative distribution of chemicals among various media (Chan *et al.*, 1986; Oliver and Kaiser, 1986; Lester and McIntosh, 1994). The lack of uptake of less lipophilic and more volatile compounds such as HCE, chlorinated toluenes, tCBs and teCBs could be attributed to the short residence time for these chemicals in bulk sediment, as was the case between field-collected versus laboratory-tested sediment samples (Table 6A). A higher percentage of the lower Kow chemicals will be found in the aqueous phases as compared to the bulk sediment phase (Kaiser *et al.*, 1985). This pattern in chemical distribution was evident in elutriates that were prepared from Station 95 sediment during a 1990 study (Bedard and Petro, 1992a). A

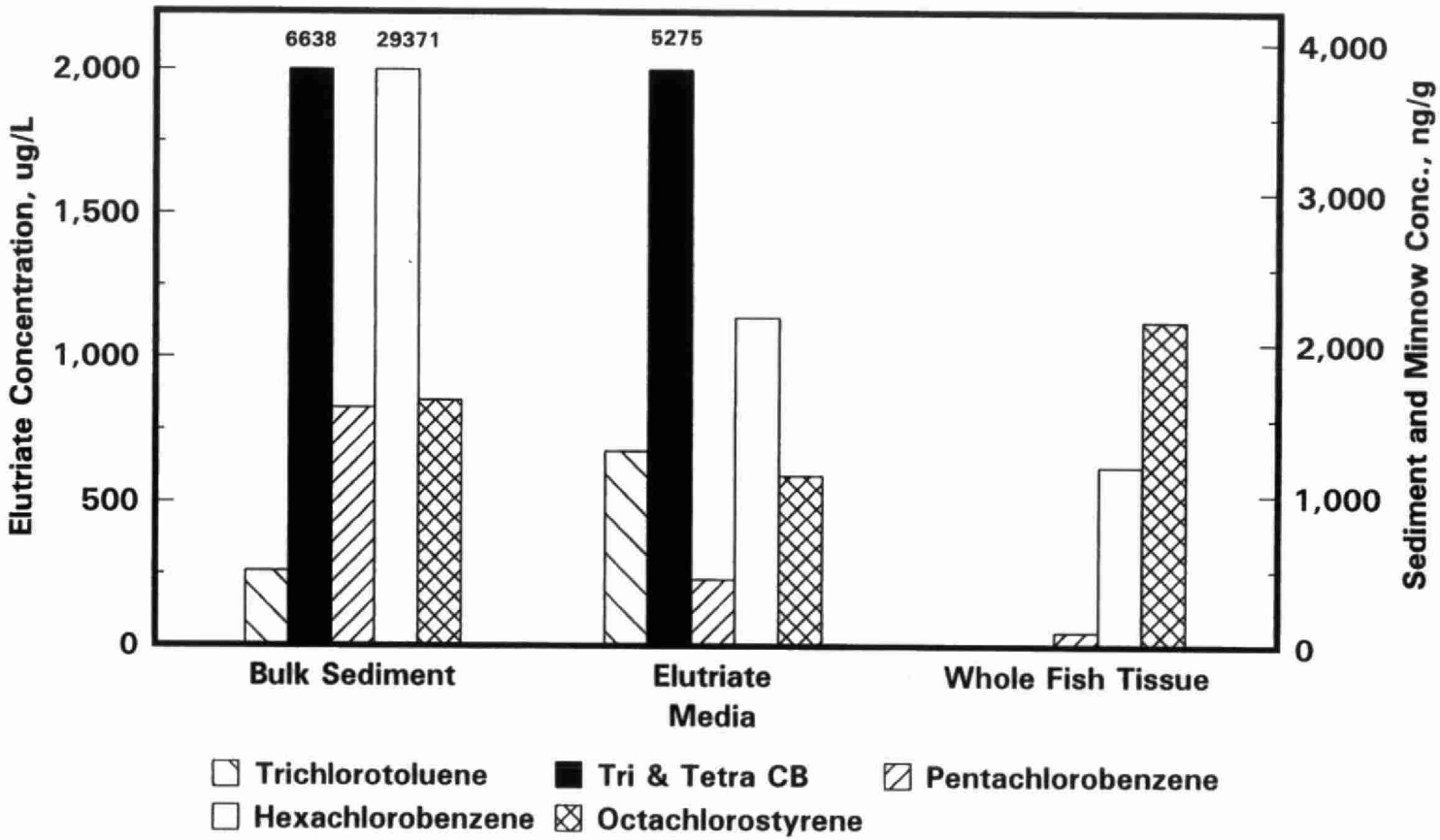
comparison of concentrations for several organic chemicals amongst bulk sediment, elutriate and fish tissue is illustrated in Figure 10. At least 54% of the total chemical composition in the elutriate consisted of tri- and tetraCBs, yet these represented only 6% of the total chemical burden in bulk sediment. The higher solubility of lower Kow chemicals increased the rate of transfer into the water column, however volatilization will further reduce exposure and uptake by even a water-column organism over time (Konemann and Van Leeuwen, 1980).

Only HCB appears to be at sufficiently high concentrations in the bulk sediment used in the preparation of the elutriate, 29371 ng/g (28% of total), to result in moderately high concentrations in the elutriate, 1138 µg/L (11% of total). Total fish tissue concentrations consisted of 37% HCB (1266 ng/g) in the 7-day elutriate exposure. In comparison, Stn 95 bulk sediment tested in 1994 indicated fish tissue HCB concentration of 36424 ng/g, an average bulk sediment HCB concentration of 80975 ng/g (omission of Stn 95-30 with no surviving minnows) and a water HCB concentration of 0.05 µg/L measured for Stn 95-30 only. Evidently, the level of sediment disturbance will influence the amount of chemical associated with suspended sediment (Schuytema *et al.*, 1988; DiToro *et al.*, 1991). This, in turn, will depend on the degree of contamination of the sediment which may trigger an avoidance response, thereby altering the degree of contact with the sediment during feeding and effect the movement of contaminants into the water-column. In fact, fish can acquire contaminants either through ingestion of suspended material and sediment particulates and/or passage through the gills in the dissolved state (Qiao and Farrell, 1996). In certain circumstances uptake may be reduced, even though sediment chemical concentrations are higher (Sijm *et al.*, 1993). The presence of HCB in the overlying water due to sediment resuspension may not necessarily mean the chemical is in an available or dissolved form for uptake (Schrap and Opperhuizen, 1990). Higher Kow compounds are less water-soluble and will desorb from suspended particulates more slowly. Schrap and Opperhuizen (1990) also propose that even minimal quantities of ingested sediment contained in the gut will affect overall whole organism tissue concentrations, particularly for more chlorinated benzenes e.g. HCB.

The chemical that showed the highest affinity for bioaccumulation in fathead minnows was OCS. Among the 12 transects tested in 1994, seven resulted in average fish OCS tissue concentrations exceeding those associated with the test sediments. Biota-sediment accumulation ratios (BSAFs) ranged from 3.0 to 12.9 at these locations. Octachlorostyrene has a log Kow of 6.2, which is the highest among the chlorinated organics examined in this study. The higher lipophicity, coupled with a longer depuration rate, increases the amount of chemical retained by the organism (Oliver, 1987; Oliver and Niimi, 1983). This tendency has been noted in field investigations for caged clams placed along the upper portion of the St. Clair River corridor for a three week period (Kauss and Hamdy, 1985). A small sample of native mussels (*Lampsilis* sp.) from the St. Clair River contained OCS at concentrations on average 52 times greater than sediment OCS concentrations, demonstrating a high degree of bioaccumulation (Pugsley *et al.*, 1985).

Tissue concentrations of surviving fathead minnows can be compared to critical body residues (CBR) and with fish flesh criteria to assess the environmental relevance of chemical availability of sediment-sorbed contaminants. The data is restricted to those chemicals selected for analysis and may only reflect a portion of those chemicals that are truly available. For this reason, the following discussion will pertain to the Dow sediments which have the highest concentrations of QCB, HCB and HCBD in both the sediment and fish. Literature

FIGURE 10. Chlorinated Organic Chemical Distribution for Bulk Sediment, Elutriate and Fathead Minnow for Station 95 (1990).



Sediment and Fish Data: dry weight

values of CBR, assuming a 5% lipid content, range from 2.5 mM/kg to 4.0 mM/kg (wet weight) (Van Hoogen and Opperhuizen, 1988; McCarty *et al.*, 1992a; Van Leeuwen *et al.*, 1992). Using an average molecular weight of 257, the resulting CBR in fish for QCB, HCB and HCBD is 4176 μg/g to 6784 μg/g (converted to dry weight). Total fish tissue concentrations for the same group of chemicals were 52 μg/g (transect 95 and 48), 14 μg/g (transect 49) and 4 μg/g (transect 96) (Table 8). The observed minnow tissue concentrations were at least two orders of magnitude lower than the predicted CBR and much lower than chronic tissue concentrations using an acute to chronic ratio of 10 (McCarty, 1986; McCarty *et al.*, 1992a). It should be noted that the analyses were carried out on surviving minnows rather than on dead animals. The latter would be more indicative of true lethal internal chemical concentrations. Carlson and Kosian (1987) provide no-effect (NOEC) tissue concentrations for HCB in fathead minnows of 97 μg/g (wet weight). Examination of 1994 tissue results using wet weight determinations revealed values well below the HCB NOEC concentration, and show little evidence of underlying stress. Once again, sites with higher minnow survival were restricted to having lower HCB sediment concentrations, therefore HCB fish tissue concentrations would be representative of less contaminated conditions.

Another set of criteria that protects against the biomagnification of organic contaminants in the food chain pertains to those concentrations measured in fish flesh. Currently, fish flesh guidelines exist for HCB (330 ng/g) and OCS (20 ng/g) based on wet weight (Newell *et al.*, 1987). Although the concentrations are specific to the removable portions of edible tissue as is routinely applied to sports fish, they have also been adopted for whole-organism young-of-the-year forage fish (Suns *et al.*, 1991). Emphasis is often placed on field collected specimens which represent natural conditions. Fathead minnow tissue concentrations obtained from static, laboratory exposures would be considered a worst-case situation and can provide insight on potential site-to-site variation in HCB and OCS chemical uptake. Each of the Dow transects resulted in minnow tissue concentrations that surpassed the fish flesh criterion for HCB (540 ng/g to 5800 ng/g, wet wt). Transect 74, situated just upstream of Dow and downstream of Polysar, also had a high minnow concentration of 880 ng/g HCB. Minnows from all of the transects where OCS was found above trace amounts exceeded the tissue OCS criterion of 20 ng/g. While the capacity for biomagnification appears to be greatest for OCS, these Dow and Polysar sediments may also pose a potential source of HCB to indigenous fish, particularly species that are resident and benthic.

Correspondence with Field Benthic Surveys

Field studies investigating the impact of contaminated sediments on indigenous macrobenthos in the St. Clair River have found positive relationships between sediment chemistry and both community and population-based parameters. Hudson and Ciborowski (1996) recently reported a greater incidence of teratogenic malformations in certain midge species at Walpole Island situated in the delta region of the St. Clair River. Toxicity results describing the spatial differences in organism survival generally paralleled those measuring adverse effects on the relative distribution and abundance of existing benthic faunal communities in 1985, 1990 and 1994 (Griffiths, 1991; OMOE, 1991; Tarandus, 1992; Farara and Burt, 1996).

5.0 CONCLUSIONS

Surficial sediment from a number of sites in the upper St. Clair River contained a wide variety of organic chemicals at measurable concentrations. Sediment concentrations of chlorinated benzenes, octachlorostyrene and mercury were dominant in sediments from the Dow area. Visual and olfactory observations for many of the ESSO, Polysar and Cole Drain samples suggested the occurrence of other petroleum or fuel-like substances and were best quantified as total petroleum hydrocarbons in bulk sediment.

The approach of using a battery of laboratory sediment toxicity tests for the assessment of spatial and temporal trends in St. Clair River sediment quality was constructive and aided in achieving specific study objectives. Among the biological endpoints, organism lethality took precedence over the observed sublethal growth effects among sites, the former being less dependent on natural factors such as substrate type. In fact, physical sediment properties did not appear to be a source of any adverse underlying stress. Of the two benthic invertebrates, the mayfly, *Hexagenia limbata*, exhibited the greatest sensitivity in terms of organism survival, while midge lethality generally concurred but to a lesser degree. Avoidance response of the mayfly appeared to be a promising test endpoint in the evaluation of sediments contaminated with organic compounds.

The fathead minnow toxicity test offered unique information in the interpretation of the toxicity data and provided useful data with respect to chemical bioaccumulation. The chemical tissue data typically supported the trends in chemical uptake for *in-situ* biota. In addition, un-ionized ammonia concentrations could have been a contributing factor for high minnow mortality at some locations.

The laboratory toxicity tests pointed out the limitation of the test method for assessing the toxicity of highly volatile substances such as hexachloroethane, trichlorobenzene and chlorotoluene. To better represent field conditions, alterations in the handling of the sediment prior to testing is recommended. This could include the elimination of the sieving procedure altogether, performing the test under reducing conditions or testing intact cores.

Overall, according to the outcome of the three independent sediment toxicity tests completed in the spring of 1994, those sediments with the most deleterious biological responses were found at Stations 44-30, 136-10, 136-30 and 95-37. Another six of the remaining 32 test sediments elicited a moderate to high degree of toxicity (> 40% mortality) to the mayfly, *Hexagenia limbata* and the midge, *Chironomus tentans* and represented areas from each of the industrial point sources which included ESSO (Stns 44-45 and 73-30), Cole Drain (Stn 45-35), Polysar (Stns 46-25 and 74-30) and Dow (Stn 48-37). The toxicity tests illustrated the high variability in organism toxicity on a spatial scale while temporal trends were fairly constant.

Chlorinated organic compounds with a higher octanol-water partitioning coefficient or Kow, as well as unidentified petroleum-based substances, are inferred as the principle causative agents that best explain the biological results for the two benthic species. Lipophilic chemicals also showed the greatest tendency for chemical uptake by fish. At several locations situated adjacent to ESSO, Cole Drain and Polysar, elevated total petroleum hydrocarbon

sediment concentrations corresponded with higher organism toxicity. Toxic effects were most frequently associated with total petroleum hydrocarbon sediment concentrations above 1500 μg/g (dry weight).

This paper represents one of the few studies that examined the effect of naturally-contaminated sediment to benthic organisms in terms of critical body residues for multiple, chlorinated organic compounds. Survival of mayfly nymphs and midge larvae negatively regressed with hexachlorobenzene, hexachlorobutadiene, octachlorostyrene and pentachlorobenzene sediment concentrations for sediments collected from Dow. The mean 10-day LC50 for the midge assay against the sum of HCB, HCBD, OCS and QCB bulk sediment concentrations was 147 μg/g (dry weight). Similarly, the mean 21-day LC50 for the mayfly test was 162 μg/g for the same group of chemicals. It is difficult to separate the exact contribution of each of these chemicals to the observed toxicity. This task could only be derived through values obtained from spiked sediment studies for single compounds and appear to be currently lacking in the literature.

REFERENCES

Adams, W.J., R.A. Kimerle and R.G. Mosher. 1985. Aquatic Safety Assessment of Chemicals Sorbed to Sediments. In R.D. Cardwell, R. Purdy and R.C. Bahner (eds) Aquatic Toxicity and Hazard Assessment: Seventh Symposium. ASTM STP 854, Philadelphia, P.A. pp. 429-453.

American Society for Testing and Material. 1995. *Standard Guide for Determination of the Bioaccumulation of Sediment-associated Contaminants by Benthic Invertebrates.* E1688-95. In Annual Book of ASTM Standards, Vol. 11.05. Philadelphia, PA. pp. 1140-1189.

Ankley, G.T., A. Katko and J.W. Arthur. 1990. Identification of Ammonia as an Important Sediment-associated Toxicant in the Lower Fox River and Green Bay, Wisconsin. *Environ. Toxicol. Chem.* 9:313-322.

Ankley, G.T., M.K. Schubauer-Berigan and J.R. Dierkes. 1991. Predicting the Toxicity of Bulk Sediments to Aquatic Organisms with Aqueous Test Fractions: Pore Water vs. Elutriate. *Environ. Toxicol. Chem.* 10:1359-1366.

Ankley, G.T., P.M. Cook, A.R. Carlson, D.J. Call, J.A. Swenson, H.F. Corcoran and R.A. Hoke. 1992. Bioaccumulation of PCBs from Sediments by Oligochaetes and Fishes: Comparison of Laboratory and Field Studies. *Can. J. Fish. Aquat. Sci.* 49:2080-2085.

Ankley, G.T., D.A. Benoit, J.C. Balogh, T.B. Reynoldson, K.E. Day and R.A. Hoke. 1994. Evaluation of Potential Confounding Factors in Sediment Toxicity Tests with Three Freshwater Benthic Invertebrates. *Environ. Toxicol. Chem.* 13:627-635.

Becker, D.S., C.D. Rose and G.N. Bigham. 1995. Comparison of the 10-day Freshwater Sediment Toxicity Test using *Hyalella azteca* and *Chironomus tentans*. *Environ. Toxicol. Chem.* 14:2089-2094.

Bedard, D.C. 1990. Factors Influencing the Bioaccumulation of Chlorinated Hydrocarbons by *Hexagenia* nymphs. Masters thesis, University of Windsor, Ontario, Canada. 201 p.

Bedard, D. and S. Petro. 1992a. *St. Clair River Study 1990 Laboratory Sediment Bioassay Report*, Ontario Ministry of Environment and Energy, Water Resources Branch, Internal Technical Report, Toronto, Ontario. 20 p.

Bedard, D. and S. Petro. 1992b. *Peninsula Harbour Study 1990 Laboratory Sediment Bioassay Report*, Ontario Ministry of Environment and Energy, Water Resources Branch, Internal Technical Report, Toronto, Ontario. 14 p.

Bedard, D. and S. Petro. 1992c. *Edna Lake Study 1990 Laboratory Sediment Bioassay Report*, Ontario Ministry of Environment and Energy, Water Resources Branch, Internal Technical Report, Toronto, Ontario. 13 p.

Bedard, D. and S. Petro. 1992d. *St. Lawrence River/Cornwall Study 1991 Laboratory Sediment Bioassay Report*, Ontario Ministry of Environment and Energy, Water Resources

Branch, Internal Technical Report, Toronto, Ontario. 17 p.

Bedard, D. and S. Petro. 1993. *Laboratory Sediment Bioassay Report on Forest Lake Sediments (1991)*, Ontario Ministry of Environment and Energy, Water Resources Branch, Internal Technical Report, Toronto, Ontario. 17 p.

Bedard, D., A. Hayton and D. Persaud. 1992. *OMOE Laboratory Sediment Biological Testing Protocol*, Ontario Ministry of the Environment, Toronto, Ontario. 23 p.

Boese, B.L., M. Winsor, H. Lee II, S. Echols, J. Pelletier and R. Randall. 1995. PCB Congeners and Hexachlorobenzene Biota Sediment Accumulation Factors for *Macoma nasuta* Exposed to Sediments with Different Total Organic Carbon Contents. *Environ. Toxicol. Chem.* 14:303-310.

Borgmann, U. and W.P. Norwood. 1993. Spatial and Temporal Variability in Toxicity of Hamilton Harbour Sediments: Evaluation of the *Hyalella azteca* 4-week Chronic Toxicity Test. *J. Great Lakes Res.* 19:72-82.

Burton, G.A., T.J. Norberg-King, C.G. Ingersoll, D.A. Benoit, G.T. Ankley, P.V. Winger, J. Kubitz, J.M. Lazorchak, M.E. Smith, E. Greer, F.J. Dwyer, D.J. Call, K.E. Day, P. Kennedy and M. Stinson. 1996. Interlaboratory Study of Precision: *Hyalella azteca* and *Chironomus tentans* Freshwater Sediment Toxicity Assays. *Environ. Toxicol. Chem.* 15:1335-1343.

Carlson, A.R. and P.A. Kosian. 1987. Toxicity of Chlorinated Benzenes to Fathead Minnows (*Pimephales promelas*). *Arch. Environ. Contam. Toxicol.* 16:129-135.

Carr, R.S., E.R. Long, H.L. Windom, D.C. Chapman, G.Thursby, G.M. Sloane and D.A. Wolfe. 1996. Sediment Quality Assessment Studies of Tampa Bay, Florida. *Environ. Toxicol. Chem.* 15:1218-1231.

Chan, C.H., Y.L. Lau and B.G. Oliver. 1986. Measured and Modeled Chlorinated Contaminant Distribution in St. Clair River Water. *Water Poll. Res. J. Canada* 21:332-343.

Ciborowski, J.J.H. and L.D. Corkum. 1988. Organic Contaminants in Adult Aquatic Insects of the St. Clair and Detroit Rivers, Ontario, Canada. *J. Great Lakes Res.* 14:148-156.

DiToro, D.M., C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Swartz, C.E. Cowan, S. P. Pavlou, H.E. Allen, N.A. Thomas and P.R. Paquin. 1991. Technical Basis for Establishing Sediment Quality Criteria for Nonionic Organic Chemicals using Equilibrium Partitioning. *Environ. Toxicol. Chem.* 10: 1541-1583.

Drouillard, K.G., J.J.H. Ciborowski, R. Lazar and G.D. Haffner. 1996. Estimation of the Uptake of Organochlorines by the Mayfly *Hexagenia limbata* (Ephemeroptera:Ephemeridae). *J. Great Lakes Res.* 22:26-35.

Environment Canada (EC). 1993. *Canadian Environmental Protection Act (CEPA), Priority Substances List Assessment Report - Hexachlorobenzene*. Government of Canada, Health and Welfare Canada and Environment Canada. Ottawa, Ontario. 52 p.

Environment Canada (EC) and Ontario Ministry of Environment (OMOE). 1986. *St. Clair Pollution Investigation (Sarnia Area).* Toronto, Ontario. 135 p.

Farara, D.G., and A.J. Burt. 1996. *Environmental Assessment of Upper St. Clair River Sediments and Benthic Macroinvertebrate Communities - 1994.* Draft Report December, 1996. Prepared for Ontario Ministry of Environment and Energy by BEAK International Incorporated, Brampton, Ontario.

Friesen, M.K. 1981. Hexagenia rigida (McDunnough). In: S.G. Lawrence (Ed.), *Manual for the Culture of Selected Freshwater Invertebrates*, Can. Spec. Publ. Fish. Aquat. Sci., 54 : 127-142.

Gobas, F.A.P.C., D.C. Bedard, J.J.H. Ciborowski and G.D. Haffner. 1989. Bioaccumulation of Chlorinated Hydrocarbons by the Mayfly (*Hexagenia limbata*) in Lake St. Clair. *J. Great Lakes Res.* 15:581-588.

Gobas, F.A.P.C., J.R. McCorquodale and G.D. Haffner. 1993. Intestinal Absorption and Biomagnification of Organochlorines. *Environ. Toxicol. Chem.* 12:567-576.

Griffiths, R.W. 1991. Environmental Quality Assessment of the St. Clair River as Reflected by the Distribution of Benthic Macroinvertebrates in 1985. *Hydrobiologia* 219:143-164.

Hanes, E.C. and J.J.H. Ciborowski. 1992. Effects of Density and Food Limitation on Size Variation and Mortality of Larval *Hexagenia rigida* (Ephemeroptera:Ephemeridae) *Can. J. Zool.* 70:1824-1831.

Harkey, G.A., P.F. Landrum and S.J. Klaine. 1994a. Comparison of Whole-sediment, Elutriate and Pore-water Exposures for use in Assessing Sediment-associated Organic Contaminants in Bioassays. *Environ. Toxicol. Chem.* 13:1315-1329.

Harkey, G.A., M.J. Lydy, J. Kukkonen and P.F. Landrum. 1994b. Feeding Selectivity and Assimilation of PAH and PCB in *Diporeia* spp.. *Environ. Toxicol. Chem.* 13:1445-1455.

Hellawell, J.M. 1986 *In*: Biological Indicators of Freshwater Pollution and Environmental Management. Eds., Elsevier Science Publishing Co., Inc., New York, New York.

Hoke, R.A., J.P. Giesy, M. Zabik and M. Unger. 1993. Toxicity of Sediments and Sediment Pore Waters from the Grand Calumet River-Indiana Harbour, Indiana Area of Concern. *Ecotoxicology Environ. Safety* 26:86-112.

Hudson, L.A. and J.J.H. Ciborowski. 1996. Spatial and Taxonomic Variation in Incidence of Mouthpart Deformities in Midge Larvae (Diptera:Chironomidae:Chironomini) *Can. J. Fish. Aquat. Sci.* 53:297-304.

International Joint Commission (IJC). 1989. *1989 Report on Great Lakes Water Quality.* Great Lakes Water Quality Board, Windsor, Ontario. 128 p.

Jaagumagi, R. 1988. The In-place Pollutants Program. Volume V, Part B. Benthic Invertebrate

Studies Results. Ontario Ministry of Environment, Toronto, Ontario. 74 p.

Jaagumagi, R., D. Bedard and S. Petro. 1996. *Sediment and Biological Assessment of the Northern Wood Preservers Inc. Site, Thunder Bay. July 1995 and September 1995.* Final Report. Ministry of Environment and Energy, Toronto, Ontario. 27 p.

Kaiser, K.L.E., M.E. Comba, H. Hunter, R.J. Maguire, R.J. Tkacz and R.F. Platford. 1985. Trace Organic Contaminants in the Detroit River. *J. Great Lakes Res.* 11:386-399.

Kauss, P.B. 1994a. *Project Description - St.Clair River Sediment Impact Zone Characterization.* Ministry of Environment and Energy. Project Code: 010011540. Etobicoke, Ontario. 14 p.

Kauss, P.B. 1994b. *Summary of St. Clair River Sediment Impact Zone Characterization Samples and Submissions.* Draft summary field notes. 5 p.

Kauss, P.B. 1994c. *Concentrations of Polychlorinated dibenzo-p-dioxins and dibenzofurans in Detroit River Surficial Sediments, 1991.* Ministry of Environment, ISBN 0-7778-3624-6. Toronto, Ontario. 13 p.

Kauss, P.B. 1995a. *Project Description - St. Clair River Sediment Impact Zone Characterization, 1995 - Sediment Traps and Contaminant Bioavailability.* Ministry of Environment and Energy. Project Code: 01001540. Etobicoke, Ontario. 14 p.

Kauss, P.B. 1995b. *Data Files on the 1994 and 1995 Sediment Quality Surveys*. Ministry of Environment and Energy.

Kauss, P.B. 1996. Ministry of Environment, Internal Technical Memorandum. May 17, 1996.

Kauss, P.B. and Y.S. Hamdy. 1985. Biological Monitoring of Organochlorine Contaminants in the St. Clair and Detroit Rivers using Introduced Clams, *Elliptio complanatus*. *J. Great Lakes Res.* 11:247-263.

Konemann, H. and K. van Leeuwen. 1980. Toxicokinetics in Fish: Accumulation and Elimination of six Chlorobenzenes by Guppies. *Chemosphere* 9:3-19.

Lake, J.L., N.I. Rubinstein, H. Lee II, C.A. Lake, J. Heltshe and S. Pavignano. 1990. Equilibrium Partitioning and Bioaccumulation of Sediment-associated Contaminants by Infaunal Organisms. *Environ. Toxicol. Chem.* 9 : 1095-1106.

Landrum, P.F. and R. Poore. 1988. Toxicokinetics of Selected Xenobiotics in *Hexagenia limbata*. *J. Great Lakes Res.* 14:427-437.

Landrum, P.F., B.J. Eadie and W.R. Faust. 1991. Toxicokinetics and Toxicity of a Mixture of Sediment-associated Polycyclic Aromatic Hydrocarbons to the Amphipod *Diporeia* sp.. *Environ. Toxicol. Chem.* 10:35-46.

Landrum, P.F., H. Lee II and M.J. Lydy. 1992. Toxicokinetics in Aquatic Systems: Model

Comparisons and use in Hazard Assessment. *Environ. Toxicol. Chem.* 11: 1709-1725.

Landrum, P.F., W.S. Dupuis and J. Kukkonen. 1994. Toxicokinetics and Toxicity of Sediment-associated Pyrene and Phenanthrene in *Diporeia* spp.: Examination of Equilibrium-partitioning Theory and Residue-based Effects for Assessing Hazard. *Environ. Toxicol. Chem.* 13:1769-1780.

Lester, D.C. and A. McIntosh. 1994. Accumulation of Polychlorinated Biphenyl Congeners from Lake Champlain Sediments by *Mysis relicta*. *Environ. Toxicol. Chem.* 13:1825-1841.

Lydy, M.J., J.T. Oris, P.C. Baumann and S.W. Fisher. 1992. Effects of Sediment Organic Carbon Content on the Elimination Rates of Neutral Lipophilic Compounds in the Midge (*Chironomus riparius*). *Environ. Toxicol. Chem.* 1:347-356.

Mackay, D. 1982. Correlation of Bioconcentration Factors. *Environ. Sci. Technol.* 16:274-278.

McCarty, L.S. 1986. The Relationship between Aquatic Toxicity QSARs and Bioconcentration for some Organic Chemicals. *Environ. Toxicol. Chem.* 5:1071-1080.

McCarty, L.S., G.W. Ozburn, A.D. Smith and D.G. Dixon. 1992a. Toxicokinetic Modeling of Mixtures of Organic Chemicals. *Environ. Toxicol. Chem.* 11:1037-1047.

McCarty, L.S., D. Mackay, A.D. Smith, G.W. Ozburn and D.G. Dixon. 1992b. Residue-based Interpretation of Toxicity and Bioconcentration QSARs from Aquatic Bioassays: Neutral Narcotic Organics. *Environ. Toxicol. Chem.* 11:917-930.

Michigan Department of Natural Resources (MDNR) and Ontario Ministry of Environment and Energy (OMOEE). 1995. *The St. Clair River Area of Concern, Water Use Goals Remedial Measures and Implementation Strategy.* Remedial Action Plan - Stage 2. March 7, 1995. Sarnia, Ontario. 121 p.

Mosher, R.G., R.A. Kimerle and W.J. Adams. 1982. *MIC Environmental Assessment Method for Conducting 14-day Partial Life Cycle Flow-through and Static Sediment Exposure Toxicity Tests with the Midge Chironomus tentans*, Report No. E5-82-M-10, Monsanto, St. Louis.

National Research Council of Canada (NRCC). 1979. Effects of Mercury in the Canadian Environment. National Research Council of Canada. Associate Committee on Scientific Criteria for Environmental Quality. NRCC Publication No. 16739. 290 p.

Nebeker, A.V., W.L. Griffis, C.M. Wise, E. Hopkins and J.A. Barbitta. 1989. Survival, Reproduction and Bioconcentration in Invertebrates and Fish Exposed to Hexachlorobenzene. *Environ. Toxicol. Chem.* 8:601-611.

Newell, A.J., D.W. Johnson and L.K. Allen. 1987. Niagara River Biota Contamination Project: Fish Flesh Criteria for Piscivorous Wildlife. New York State Department of Environmental Conservation. Technical Report 87-3.

Odin, M., A. Feurtet-Mazel, F. Ribeyre and A. Boudou. 1994. Actions and Interaction of Temperature, pH and Photoperiod on Mercury Bioaccumulation by Nymphs of the Burrowing Mayfly *Hexagenia rigida*, from the Sediment Contamination Source. *Environ. Toxicol. Chem.* 13:1291-1302.

Oliver, B.G. 1987. Biouptake of Chlorinated Hydrocarbons from Laboratory-spiked and Field Sediments by Oligochaete Worms. *Environ. Sci. Technol.* 21:785-790.

Oliver, B.G. and A.J. Niimi. 1983. Bioconcentration of Chlorobenzenes from Water by Rainbow Trout: Correlations with Partition Coefficients and Environmental Residues. *Environ. Sci. Technol.* 17:287-291.

Oliver, B.G. and R.A. Bourbonniere. 1985. Chlorinated Contaminants in Surficial Sediments of Lakes Huron, St. Clair and Erie: Implications Regarding Sources along the St. Clair and Detroit Rivers. *J. Great Lakes Res.* 11:366-372.

Oliver, B.G. and A.J. Niimi. 1985. Bioconcentration Factors of Some Halogenated Organics for Rainbow Trout: Limitation in their use for Prediction of Environmental Residues. *Environ. Sci. Technol.* 19:842-849.

Oliver, B.G. and K.L. Kaiser. 1986. Chlorinated Organics in Nearshore Waters and Tributaries of the St. Clair River. *Water Poll. Res. Can.* 21:344-350.

Ontario Ministry of the Environment (OMOE). 1977. *St. Clair River Organics Study Biological Surveys 1968 and 1977.* Southwestern Region, London, Ontario. 90 p.

OMOE. 1983. *Handbook of Analytical Methods for Environmental Samples*. Vol. 1 and 2. Laboratory Services and Applied Research Branch, Toronto, Ontario.

OMOE. 1989. *A Guide to the Collection and Submission of Samples for Laboratory Analysis.* Laboratory Services Branch, Toronto, Ontario. 81 p.

OMOE. 1990. *The Determination of Polychlorinated Biphenyls (PCB), Organochlorines (OC), and Chlorobenzenes (CB) in Fish and Clams by GLC-ECD.* PFAOC-E3136A. Laboratory Services Branch, Etobicoke, Ontario. February 19, 1990. 45 p.

OMOE. 1991. *St. Clair River MISA Pilot Site Investigation.* Volume II. Part II-Detailed Technical Findings. Toronto, Ontario.

OMOE. 1992a. *Report on the 1990 Industrial Direct Discharges in Ontario*. Ontario Ministry of the Environment, Queen's Printer for Ontario, Toronto, Ontario.

OMOE. 1992b. *Candidate Substances List for Bans or Phase-outs*. Ontario Ministry of Environment, Hazardous Contaminants and Water Resources Branch, Toronto, Ontario. 63 p.

OMOEE. 1994a. *The Determination of Trace Metals in Sediments by Spectro Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES).* HMARSOIL-E3062A. Laboratory Services Branch, Etobicoke, Ontario. March 28, 1994. 45 p.

OMOEE. 1994b. *The Determination of Polychlorinated Biphenyls (PCBs), Organochlorines (OCs), and Chlorobenzenes (CBs) in Soil and Sediments by Gas Liquid Chromatography-Electron Capture Detection (GLC-ED).* PSAOC-E3270A. Laboratory Services Branch, Etobicoke, Ontario. July 18, 1994. 37 p.

OMOEE. 1994c. *The Determination of Polynuclear Aromatic Hydrocarbons (PAH) in Soil and Sediments by Gel Permeation Chromatography-High Performance Liquid Chromatography (GPC-HPLC).* PSAPAH-E3350A. Laboratory Services Branch, Etobicoke, Ontario. July 20, 1994. 28 p.

OMOEE. 1994d. *Water Management Policies, Guidelines, Provincial Water Quality Objectives of the Ministry of Environment and Energy,* Toronto, Ontario. 30 p.

OMOEE. 1995a. *The Determination of Total Carbonate-Carbon in Soil and Sediments by Coulometry.* CARBONAT-E3012A. Laboratory Services Branch, Etobicoke, Ontario.

OMOEE. 1995b. *The Determination of Particle Size on Sediments by MICROTRAC Particle Size Analyzer Model 7991-2.* SMPART-E3128A. Laboratory Services Branch, Etobicoke, Ontario.

OMOEE and MDNR. 1993. *St.Clair River Remedial Action Plan, Stage 1 Addendum.* Prepared by Geomatics International. Sarnia, Ontario. 124 p.

Persaud, D., R. Jaagumagi and A. Hayton. 1992. *Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario.* Ontario Ministry of the Environment, Toronto. 30 p.

Platford, R.F., R.J. Maquire, R.J. Tkacz, M.E. Comba and K.L.E. Kaiser. 1985. Distribution of Hydrocarbons and Chlorinated Hydrocarbons in Various Phases of the Detroit River. *J. Great Lakes Res.* 11:379-385.

Pope, R.J. 1993. *Assessment of 1990 St. Clair River Benthic-Macroinvertebrate Communities Relative to Sediment Quality,* Tarandus Associates, Brampton, Ontario. 124 p.

Pugsley, C.W., P.D.N. Hebert, G.W. Wood, G. Brotea and T.W. Obal. 1985. Distribution of Contaminants in Clams and Sediments from the Huron-Erie Corridor. I-PCBs and Octachlorostyrene. *J. Great Lakes Res.* 11:275-289.

Qiao, P., and A.P. Farrell. 1996. Uptake of Hydrophobic Xenobiotics by Fish in Water Laden with Sediments from the Fraser River. *Environ. Toxicol. Chem.* 15:1555-1563.

Reuber, B., D. Mackay, S. Paterson and P. Stokes. 1987. A Discussion of Chemical Equilibria and Transport at the Sediment-water Interface. *Environ. Toxicol. Chem.* 6:731-739.

Russo, R.C. 1985. Ammonia, Nitrite and Nitrate. *In*: Fundamentals of Aquatic Toxicology, Eds., G.M. Rand and S.R. Petrocelli, Hemisphere, Washington, D.C., pp. 455-471.

Sarda, N. and G.A. Burton, Jr. 1995. Ammonia Variation in Sediments: Spatial, Temporal and

Method-related Effects. *Environ. Toxicol. Chem.* 14:1499-1506.

SAS. 1985. Statistical Analysis Systems, *SAS/STAT User's Guide*, Version 6.03 Edition, SAS Institute, Cary, S.C.

Schrap, S.M. and A. Opperhuizen. 1990. Relationship between Bioavailability and Hydrophobicity: Reduction of the Uptake of Organic Chemicals by Fish due to the Sorption on Particles. *Environ. Toxicol. Chem.* 9:715-724.

Schubauer-Berigan, M.K., B.D. Monson, C.W. West and G.T. Ankley. 1995. Influence of pH on the Toxicity of Ammonia to *Chironomus tentans* and *Lumbriculus variegatus*. *Environ. Toxicol. Chem.* 14:713-717.

Schuytema, G.S., D.F. Krawczyk, W.L. Griffis, A.V. Nebeker, M.L. Robideaux, B.J. Brownawell and J.C. Westall. 1988. Comparative Uptake of Hexachlorobenzene by Fathead Minnows, Amphipods and Oligochaete Worms from Water and Sediment. *Environ. Toxicol. Chem.* 7:1035-1045.

Sijm, D.T.H.M., M. Schipper and A. Opperhuizen. 1993. Toxicokinetics of Halogenated Benzenes in Fish: Lethal Body Burden as a Toxicological Endpoint. *Environ. Toxicol. Chem.* 12:1117-1127.

Steel, R.G.D. and J.H. Torrie. 1960. Principles and procedures of statistics. McGraw-Hill Book Company Inc., New York, 481 p.

Stehly, G.R., P.F. Landrum, M.G. Henry and C. Klemm. 1990. Toxicokinetics of PAHs in *Hexagenia*. *Environ. Toxicol. Chem.* 9:167-174.

Stephan, C.E. 1977. Methods for Calculating an LC50, In: F.L. Mayer and J.L. Hamelink (Eds.) *Aquatic Toxicology and Hazard Evaluation*, ASTM STP 634, Philadelphia PA, pp.65-84.

Suedel, B.C. and J.H. Rodgers, Jr. 1994. Responses of *Hyalella azteca* and *Chironomus tentans* to Particle-size Distribution and Organic Matter Content of Formulated and Natural Freshwater Sediments. *Environ. Toxicol. Chem.* 13:1639-1648.

Suns, K., G. Hitchin and D. Toner. 1991. Spatial and Temporal Trends of Organochlorine Contaminants in Spottail Shiners (*Notropis hudsonius*) from the Great Lakes and their Connecting Channels (1975-1988). Ministry of Environment report ISBN 0-7729-8411-5, Toronto, Ontario.

Tarandus Associates Limited. 1992. *Analysis of the 1990 Benthos Samples from the St. Clair River*. Prepared for the Ontario Ministry of the Environment, Southwestern Region by Tarandus Associates Limited. 39 p.

Thomann, R.V., J.P. Connolly and T.F. Parkerton. 1992. An Equilibrium Model of Organic Chemical Accumulation in Aquatic Food Webs with Sediment Interaction. *Environ. Toxicol. Chem.* 11:615-629.

Thurston, R.V., R.C. Russo and G.R. Phillips. 1986. Acute Toxicity of Ammonia to Fathead Minnows. *Trans. American Fisheries Society* 112:705-711.

Townsend, B.E., S.G. Lawrence and J.F. Flannagan. 1981. Chironomus tentans (Fabricius). In: S.G. Lawrence (Ed.), *Manual for the Culture of Selected Freshwater Invertebrates*, Can. Spec. Publ. Fish. Aquat. Sci., Vol. 54, pp. 127-142.

Upper Great Lakes Connecting Channels Study (UGLCCS). 1988. *Final Report of the Upper Great Lakes Connecting Channels Study.* Ontario Ministry of Environment, Environment Canada, US EPA and Michigan Department of Natural Resources. Vol. 2.

U.S. Environmental Protection Agency. 1987. *Guidelines for the Culturing of Fathead Minnows Pimephales promelas for use in Toxicity Tests.* EPA-600-3-87-001. Environmental Research Laboratory, Duluth, MN, 42 pp.

Van Hoogen, G. and A. Opperhuizen. 1988. Toxicokinetics of Chlorobenzenes in Fish. *Environ. Toxicol. Chem.* 7:213-219.

Van Leeuwen, C.J., P.T.J. Van Der Zandt, T. Aldenberg, H.J.M. Verhaar and J.L.M. Hermens. 1992. Application of QSARs, Extrapolation and Equilibrium Partitioning in Aquatic Effects Assessment. I. Narcotic Industrial Pollutants. *Environ. Toxicol. Chem.* 11:267-282.

Veith, G.D., D.J. Call and L.T. Brooke. 1983. Structure-Toxicity Relationships for the Fathead Minnow, *Pimephales promelas*: Narcotic Industrial Chemicals. *Can. J. Fish. Aquat. Sci.* 40:743-748.

APPENDIX

TABLE A1. Analytical detection limits for nutrients, inorganic and organic contaminants in sediment and biota samples.

Parameter	Sediment (units: dry weight)	Parameter	Sediment (units: dry weight)	Biota (unit: wet weight)
Nutrient :		Organic :		
Loss on Ignition	1.0 mg/g	Total PCBs	20 ng/g	20 ng/g
Total Organic Carbon	0.2 mg/g	Heptachlor	1 ng/g	1 ng/g
Total Kjeldahl Nitrogen	0.025 mg/g	Aldrin	1 ng/g	1 ng/g
Total Phosphorus	–	Mirex	5 ng/g	5 ng/g
		a–BHC	1 ng/g	1 ng/g
Trace Metal :		b–BHC	1 ng/g	1 ng/g
		g–BHC	1 ng/g	1 ng/g
Arsenic	–	a–Chlordane	2 ng/g	2 ng/g
Cadmium	0.05 µg/g	g–Chlordane	2 ng/g	2 ng/g
Chromium	1.0 µg/g	Oxychlordane	2 ng/g	–
Copper	0.5 µg/g	op–DDT	5 ng/g	5 ng/g
Iron	200 µg/g	pp–DDD	5 ng/g	5 ng/g
Lead	1.25 µg/g	pp–DDT	5 ng/g	5 ng/g
Mercury	0.01 µg/g	pp–DDE	5 ng/g	5 ng/g
Nickel	0.2 µg/g	Methoxychlor	5 ng/g	–
Zinc	2.0 µg/g	Heptachlor epoxide	1 ng/g	–
		Endosulphan I	2 ng/g	–
Organic:		Dieldrin	2 ng/g	–
		Endrin	4 ng/g	–
Naphthalene	20 ng/g	Endosulphan II	4 ng/g	–
Acenapthylene	20 ng/g	Endosulphan Sulphate	4 ng/g	–
Acenaphthene	20 ng/g	Hexachloroethane	1 ng/g	1 ng/g
Fluorene	20 ng/g	Hexachlorobutadiene	1 ng/g	1 ng/g
Phenanthrene	20 ng/g	2,3,6–trichlorotoluene	1 ng/g	1 ng/g
Anthracene	20 ng/g	2,4,5–trichlorotoluene	1 ng/g	1 ng/g
Fluoranthene	20 ng/g	2,6,5–trichlorotoluene	1 ng/g	–
Pyrene	20 ng/g	1,2,3–trichlorobenzene	2 ng/g	2 ng/g
Benzo[a]anthracene	20 ng/g	1,2,4–trichlorobenzene	2 ng/g	2 ng/g
Chrysene	20 ng/g	1,3,5–trichlorobenzene	2 ng/g	2 ng/g
Benzo[b]fluoranthene	20 ng/g	1,2,3,4–tetrachlorobenzene	1 ng/g	1 ng/g
Benzo[k]fluoranthene	20 ng/g	1,2,3,5–tetrachlorobenzene	1 ng/g	1 ng/g
Benzo[a]pyrene	40 ng/g	1,2,4,5–tetrachlorobenzene	1 ng/g	1 ng/g
Benzo[g,h,i]perylene	40 ng/g	Pentachlorobenzene	1 ng/g	1 ng/g
Dibenzo[a,h]anthracene	40 ng/g	Hexachlorobenzene	1 ng/g	1 ng/g
Indeno[123–cd]pyrene	40 ng/g	Octachlorostyrene	1 ng/g	1 ng/g
		Toxaphene	–	200 ng/g